TO MY FATHER

A NATIONWIDE INVESTIGATION OF SULFURIC ACID PRODUCTION

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By
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I certify that I have read this thesis and that in my opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

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ABSTRACT

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In this thesis, the production, consumption, demand, raw materials, prices, plant costs, production methods of sulfuric acid are investigated on a nation-wide scale and also abroad.

As the trade of sulfuric acid inland and abroad is investigated, the related prices are noted in order to enlighten the views of production possibilities.

For full understanding of the situation, the past production, consumption and tendency to consume in the near future are studied comparing with the other nations. At this point, since the share of fertilizer sector on sulfuric acid consumption is the greatest, more attention is paid to this sector.

For the forecast of sulfuric acid requirement in the next ten years, three approaches are done including an econometric trend analysis.

Due to its costly and difficult transportation, sulfuric acid plants are built near the cons umption centers. The raw material availabilty is an important factor in deciding on an investment of sulfuric acid plant.

Therefore, raw material situation in Turkey and in the world is included with the supply forecast for ten years.

In the thesis, the historical evolution of production methods and recent modifications to plant design form one chapter. Sulfuric acid plants may create troublesome air pollution, in this respect environment control and cost of control in sulfuric acid plants are investigated.

The prices of sulfuric acid andits raw materials in Turkey and abroad are included in this thesis.

As an indication or guideline for investment in sulfuric acid production, the plant costs for various raw material based plants are comparatively investigated as they are adopted to Turkey's market conditions..

The thesis concludes with the proposals related to production methods, raw materials, cost of plant, regional location of the plant and the Governmental promotive measures to be taken for the effective and economic utilization of existing national sources.

In the appendices, information related to the strength of sulfuric acid, Turkish Standards, materials of construction, storing, loading and unloading of sulfuric acid, unit consumption data in various industries and international patents are included.

ÖZET

SÜLFÜRİK ASİT ÜRETİMİNİN YURT ÇAPINDA DEĞERLENDİRİLMESİ ARAŞTIRMASI

Bu tezde, sülfürik asitin yurt içinde ve dışında üretim, tüketim, talep durumu ile hammaddeleri, fiyatları, yatırım tutarları ve üretim metotları araştırılmıştır.

Sülfürik asitin yurt içi ve yurt dışı ticareti incelenirken, üretim imkânlarına ışık tutması amacıyla fiyatları da verilmiştir.

Durumun bütünüyle anlaşılabilmesini teminen, geçmiş üretim ve tüketim yanında, yakın gelecekte tüketim temayülünün ne olacağı diğer ülkelerle kıyaslanarak araştırılmıştır. Bu arada, sülfürik asit tüketiminde işgal ettiği büyük hisse açısından gübre sanayiine önem verilmiştir.

Önümüzdeki on yıl ihtiyacının tesbitine bir ekonometrik analiz de dahil olmak üzere üç yaklaşımla bakılmıştır.

Masraflı ve zor taşınmasından dolayı sülfürik asit tesisleri, tüketim merkezlerine yakın kurulmaktadır. Yatırım kararının alınmasında hammadde varlığı önemli bir etken olmaktadır. Bu nedenlerle bugünkü Türkiye ve

Dünya hammadde durumu ile trend tahminlerine yer verilmiştir.

Tezde, üretim metotlarının tarihi gelişimi ve son modifikasyonları bir bahis teşkil etmektedir. Sülfürik asit tesisleri ciddî hava kirliliği problemleri yaratabilmektedir. Bu açıdan, sülfürik asit tesislerinde çevre kontrolü ve maliyeti incelenmiştir.

Sülfürik asit üretiminde yapılacak yatırımlar için bir gösterge niteliğinde olmak üzere, çeşitli hammaddelere dayalı tesislere ait yatırım tutarları Türkiye pazar durumuna göre revize edilerek mukayaseli incelenmiştir.

Sonuçta, üretim metoduna, hammaddelere, yatırımın maliyetine, tesis kuruluş bölgesine ve icra organlarınca alınması gerekli teşvik tedbirlerine ilişkin mevcut millî kaynakların ekonomik ve verimli olarak kullanılmasına yönelik öneriler yer almaktadır.

Tezin ekinde, sülfürik asitin konsantrasyonuna, Türk Standardlarına, sülfürik asit tesislerinde kullanılan malzemeye, sülfürik asitin depolanması, yüklenmesi ve boşaltılmasına, çeşitli sanayilerde birim kullanım miktarlarına ve uluslararası patentlerine ilişkin bilgiye yer verilmiştir.

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NOMENCLATURE

Symbol	Description
AET	Avrupa Ekonomik Topluluğu
AS	Amonyum sülfat gübresi
^{o}Bé	Degrees Baumé
CAN	Calcium amonium nitrate
CF	cubic feet
CIF	Cost-insurance-freight
DAP	Diammoniumphosphate
DC/DA	Double catalysis/double absorption
DDT	Dimethyldiphenyl trichloro ethane
DM	Deutsche Mark
DPT	Devlet Planlama Teşkilatı
EEC	European Economic Community
ECN	European Chemical News
FOB	Freight-on-board
GB	Great Britain
KBI	Karadeniz Bakır İşletmeleri
kwh	kilowatt-hour
MKE	Makina ve Kimya Endüstrisi
MTAE	Maden Tetkik ve Arama Enstitüsü
n.a	not available
NPK	Nitrogen-phosphorus-potasium
NSP	Normal superphosphate
OECD	Organization for Economic Cooperation and Development

ÖİK	Özel İhtisas Komisyonu
ppm	parts per million
scf	standard cubic feet
SPO	State Planning Organization
ST/D	short tons per day
T/D	tons per day
TL	Turkish Lira
tpd	tons per day
tpy	tons per year
TSP	Triple superphosphate
UNIDO	United Nations Industrial Development Organization
UK	United Kingdom
USA	United States of America
USSR	United Soviet Socialist Republic

INTRODUCTION

Sulfuric acid is the number one chemical in terms of both production value and tonnage of production. Among inorganic chemicals it ranks well ahead of ammonia, caustic and chlorine. It also ranks well ahead of number one organic chemical, ethylene.

Many authors agree that sulfuric acid is of such a paramount significance that the per capita use of sulfuric acid is an index of the technical development of a nation, in other words the amount consumed reflects the industrial activity of a nation.

Sulfuric acid is not a one-function or one-purpose product. It is used as a drying agent, acidifying agent (pH control), hydrolyzing agent, neutralizing agent, concentrating agent, dehydrating agent, oxidizing agent, polymerizing agent, purifying agent, absorbing agent, leaching agent, catalyst and active reagent in petrochemical and inorganic chemical process.

Sulfuric acid is not a one-strength product. It is used in a wide range of strengths from very dilute concentrations for pH control to the strong fuming acids used in the dye, explosives, detergent, pharmaceutical and petrochemical industries.

Sulfuric acid is not a one-quality product.

It is produced and supplied in exact purities for storage batteries, rayon, textile, dye, food and pharmaceutical industries, in less pure grades for steel, heavy chemical, petrochemical, fertilizer, superphosphate and ammonium sulfate industries.

Sulfuric acid need not be a one-time-use product. It can be recovered easily from some phases in the refining of petroleum and in the manufacture of explosives, petrochemicals, detergents and dyes. It is often recovered in a form unsuitable for re-use in the same process but of a strength and quality suitable for use in another process. Sulfuric acid can also be returned to the producer for fortification with sulfur trioxide or for regeneration to strong acid.

Industries which are the principal users of sulfuric acid includes: the wet process phosphoric acid industry which is on the route to produce many phosphate fertilizers, in petroleum refining, the production of alcohols, the production of ammonium sulfate, and in the production of normal superphosphate (the usual use of chamber acid which is more dilute than the acid normally produced by contact plants), also, iron and steel pickling caprolactam, production of surface active agents, production of methylmethacrylate, production of hydrofluoric acid and the production of alumium sulfate. Industries which do not use up the sulfur values is approximately 10 % of the total quantity of acid used, the remainder being supplied from regenerated or reconstituted acid produced from dilute acid from the plant operation. Large amounts of dilute sulfuric acid recovered from smelter operations are also used in leaching operations to produce ore concentrates used in the smelters.

The aim of this thesis is to investigate the production, consumption and demand for this multipurpose chemical, sulfuric acid in Turkey. This requires the investigations of its raw materials and the situation in the World Market as well. It is expected from the thesis to come to a conclusion on the type of plant to be established to meet the deficit according to the demand projections, on the technology applied there, the raw material used, cost of the plant, capacity of the plant and the start-up date.

It is hoped that the thesis is the beginner of such investigations of chemicals separately. During the preparation of the thesis all the related Turkish Authorities are contacted and all possible information taken. Here it is seen that independent surveys of chemicals are lacking which is considered as a gap during the stages of economic development in Turkey.

CHAPTER 1

WORLD PRODUCTION AND TRADE IN SULFURIC ACID

In 1971 world production of sulfuric acid reached an estimated level of 86 million tons of which Europe accounted for about 47 % and the United States for about 30 % (59, 120, 136). As can be seen from Table 1. The most rapid expansion of sulfuric acid production continued to take place in the socialist countries of eastern Europe, even though in these countries the pace of annual growth slowed down in the second half of the 1960's.

Taking into account the industrial countries the highest annual rates of growth during the decade were registered in Bulgaria (16.8 %), Finland (15 %), Greece (19 %), Norway (13 %), Romania (15.5 %) and Hungary and Poland (more than 12 %) (153,154).

Trade in sulfuric acid continued to be relatively small on account of the high cost of transportation (Table 2).During the decade imports and exports were rather irregular due to the fact that on the one hand, consumers were ready to bear the high cost of transport only in the case of an acute shortage of the product and, on the other hand, to the fact that the demand is still largely dependent on the fertilizer sector, which is a rather unstable sector. (115)

With regard to the geographical pattern of trade, owing to the high cost and to the danger arising from its transport, trade in sulfuric acid is generally limited to movements across borders.

The most important outlet for sulfuric acid continued to be the fertilizer sector, namely phosphatic fertilizers and ammonium sulfate. However, in the more industrialized countries this relationship is becoming less close since applications of sulfuric acid have become more diversified and therefore its utilization by other economic sectors. has grown (Table 5).

In the European countries still in the process of industrialization, between 70 and 90 % of sulfuric acid is consumed for the production of fertilizers (Table 6), while in the industrialized countries only between 25 and 50 % is used for this purpose. The importance of other consuming sectors such as paint and pigments, detergents and soaps, dyestuffs and intermediates, natural and man-made fibres has been in fact growing steadily during the decade.

The construction of large size plants will become a more widespread feature of the sulfuric acid industry. Countries such as Hungary, Poland, and Spain are planning to have plants of 200,000-300,000 tons capacity in the near future. In the United States and in a number of European countries, small plants that are still in existence will be replaced by large plants for economic reasons .

Supplies of raw materials are at present plentiful, and prices are competitive. These factors should assure a high level of activity of all operating plants.

TABLE 1 : WORLD PRODUCTION OF SULFURIC ACID (100 %)

(1000 metric tons) (9,10,15,40,45,60,
61,65,66,97,98,
120,134,135,137,
138,150)

Countries	1964	1965	1966	1967	1968	1969	1970	1971
Argentina	151	162	149	154	162	184	185	162
Austria								311
Australia	1476	1656	1800	2028	1920	1884	1704	1524
Belgium	1344	1488	1368	1488	1740	1836	1812	1824
Brazil	300	298	300	365	367	420		
Bulgaria	290	318	353	360	472	498	516	500
Canada	1764	1397	2268	2496	2592	2172	3348	2580
China	126	187	180	193	216	251	280	247
Cuba	193	202	230	270	313			
Czechoslavakia	893	934	983	1012	977	1033	1140	1151
Denmark						22	22	17
Egypt	170	194	212	229	260	290	298	
Finland	355	383	480	550	595	673	842	779
France	2700	2916	3072	3228	3348	3528	3720	3816
Germany (East)	937	985	973	988	1078	1104	1135	1092
Germany (West)	3600	3760	3840	3780	4210	4480	4392	4344
Greece	120	138	236	379	504	551	665	
Hungary	339	394	418	451	469	479	490	454
India	679	685	690	804	984	1121	1043	1078
Israel	159	156	158	166	187	185	206	185
Italy	2892	2976	3372	3528	3312	3360	3288	3108
Japan	5376	5652	6036	238	6588	6756	6888	6732
Mexico	433	508	580	640	731	1067	1304	1420
Netherlands	972	1092	1056	1164	1380	1512	1524	1476

TABLE 1. Cont'd.

Countries	1964	1965	1966	1967	1968	1969	1970	1971
Neth.Antilles			149	141	132			
Norway	109	125	139	214	262	311	283	259
Pakistan	22	23	24	24	33	34	41	40
Phillippines	38	41	37	166	205	174	199	244
Poland	996	1068	1140	1212	1320	1512	1932	2184
Portugal	408	413	412	403	431	464	210	310
Romania	416	541	619	679	773	838	990	1031
Spain	1524	1620	1776	1800	2064	2148	2040	1860
Sweden	524	580	602	604	632	703		
Switzerland						138	141	143
Tunisia			393	372	413	380	426	434
Turkey	2[illegible]	20	25	28	28	55	56	64
USSR	7644	8520	9372	9732	10164	10668	12252	12348
United Arap Rep.			213	229	260			
United King.	3180	3360	3168	3228	3336	3288	3384	3432
United States	20796	22548	25752	26136	25896	26797	26676	26400
Yugoslavia	473	436	542	462	460	544	667	769
TOTAL	62600	67740	73777	76960	79850	82880	85980	86671

TABLE 2 : IMPORTS AND EXPORTS OF SULFURIC ACID INCLUDING OLEUM IN EUROPE, THE UNITED STATES OF AMERICA AND JAPAN IN 1969, 1970 and 1971 (metric tons) (154)

COUNTRIES	IMPORTS			EXPORTS		
	1969	1970	1971	1969	1970	1971
Austria	14074	11294	31346	158	501	254
Belgium-Luxemburg	156762	218544	285732	9805	156587	142843
Bulgaria	195	-	-	64442	10340	21203
Denmark	3629	3745	3802	7621	7540	28
Fed.Rep.of Germany	109590	164998	110363	157806	100711	279937
Finland	30	33	15584	4211	74309	36569
Hungary	61623	73136	53637	109	337	4511
Italy	14532	26822	42694	114229	83762	10352
Netherlands	25000	43000	55000	109000	145000	116000
Norway	881	1062	41384			
Poland	4768			14986	126123	197373
Portugal	46	47	54	28385	31351	18389
Spain	22034	18053	21475	10152	5	6682
Switzerland	860	1051	1555	12748	13645	15035
Turkey	12362	51618	108439			
United Kingdom	312658	300215	196135	2821	1779	10288
Yugoslavia	140	356	1014	41429	41084	27316
United States	89534	134001	123458	44874	36928	22905

TABLE 5 : USA SULFURIC ACID (100 %) Market Data (46)

	1969	1970	1971
Domestic production (1000 short tons)	29,557	29,577	29,400
Export (1000 short tons)	49,5	36,9	50,5
value at port (mil. $)	1.715	1.759	0.947
Imports (1000 short tons)	98,8	147,6	136,1
value in foreign country (mil. $)	1,881	2,936	3,257
Consumed at plant (1000 short tons)	16,500	16,900	17,400
Apparent Consumption (1000 short tons)	29,586	29,687	29,486

TABLE 4 : SULFURIC ACID (100 %) PRODUCTION IN COMMON MARKET COUNTRIES
(136, 137, 157) (1000 metric tons)

Country	1953	1958	1960	1963	1964	1965	1966	1967	1968	1969	1970	1971
W. Germany	1897	2917	3170	3316	3602	3751	3834	3778	4210	4481	4435	4388
France	1180	1824	1983	2394	2702	2916	3073	3227	3349	3527	3682	3923
Italy	1501	2031	2299	2711	2890	2979	3369	3524	3489	3465	3327	3097
Netherlands	584	761	862	854	976	1090	1058	1170	1376	1511	1563	1496
Belgium	767	1133	1404	1249	1348	1488	1362	1484	1746	1837	1794	1932
Luxemburg	-	-	-	-	-	-	-	-	-	-	-	-
EEC Total	6029	8666	9718	10524	11518	12224	12696	13183	14170	14821	14804	14836

TABLE 5 : USA SULFURIC ACID CONSUMPTION (%)
(47, 166)

	1957		1960	1968
	1000 tons	%	%	%
Fertilizer				
-superphosphate	4550	26.6	30.6	35.7
-ammoniumsulfate	1600	9.3	6.1	6.8
Fertilizer total	6150	35.9	36.7	42.5
Inorganic pigments	1380	8.1	7.7	5.9
Metallurgy	1290	7.4	9.9	6.1
Fibres, rayon and film	780	4.6	2.1	3.1
Others	5520	32.3	43.6	42.4
Grand Total	15120	100.0	100.0	100.0

TABLE 6 : SULFURIC ACID END USES (%) IN WESTERN EUROPE, 1969 (65)

Industry	W.Germany	France	Italy	Netherlands	Belgium	United Kingdom
Fertilizers	36	55	54.3	73.5	48	38.5
Textile Industry and cellulose films	6	4.6	7.3	2.9	2	4
Pickling and mechanical engineering	3.2	3.3	2.5	0.3	2	3.9
Pigments	17	7.6	6.3	5.9	3	17.5
Petroleum Industry	1	1.3	0.2	0.8	1	1.8
Chemical Industry (including petrochemicals)	26.9	26.1	24.9	16.6	42	23.9
Other Uses	9.9	4.1	4.5	-	2	10.4
	100.0	100.0	100	100.0	100.0	100.0

TABLE 7 : SULFURIC ACID CONSUMPTION BY END USES IN VARIOUS COUNTRIES (%) (120)

FINLAND	1968	1969
Fertilizers	47	44
Titanium dioxide	25	28
Paper and Cellulose	6	6
Rayon	5	5
Mining	3	5
Others	14	12
	100	100

SPAIN	1969
Fertilizers	67
Inorganic products	11
Pigments	4
Explosives	3
Chemical Fibres	2
Others	13
	100

POLAND	1960	1970	Future
Fertilizers	45	50	69
Synthetic fibres	9	5	5
Steel pickling	23	10	8
Others	23	35	18
	100	100	100

In Sweden and in Yugoslavia the consumption of sulfuric acid for making fertilizers amounted to 40 and 72 per cent respectively of the total.

TABLE 8 : UNITED KINGDOM SULFURIC ACID AND OLEUM CONSUMPTION (metric tons of 100 % acid)

(16)

End Use	1970	% change over 1969
Fertilizer and Agriculture	1,158,428	2.7
Ammonium sulfate	266,825	
Phosphate Fertilizers	910,399	
Paints and Pigments	606,510	9.1
Transparent Cellulose film	522,086	6.2
Chemicals	442,509	
Plastics	127,010	
Sulfates (Al,Ba,Cu,Mg,Zn)	97,499	
Hydrofluoric Acid	63,383	
Hydrochloric Acid	49,402	
Soap and Detergents	370,780	3.8
Metallurgy	124,260	7.7
Steel Pickling	117,638	
Dyestuffs and Intermediates	122,635	0.4
Petroleum	53,872	-7.1
Other	321,705	-3.0
Exports	567	
Total	3,712,785	1.2

Total 100% acid capacity in 1970:

4,074,890 in tpy

Raw materials used :

-imported sulfur	58.8 %
-pyrite	7.5 %
-anhydrite	18.7 %
-zinc concentrates	8.1 %
-spent oxide	2.8 %
-oil-recovered material	3.3 %

TABLE 9 : ITALIAN SULFURIC ACID DATA (98 % acid) (9)

PRODUCTION, metric tons	TOTAL	CONTACT	CHAMBER
1961	2,445,585	1,435,290	1,010,296
1962	2,550,507	1,560,094	990,413
1963	2,710,836	1,816,360	894,476
1964	2,890,299	2,035,222	805,077
1965	2,978,890	2,141,541	837,349
1966	3,369,203	2,519,076	850,127
1967	3,523,757	2,687,798	835,959
1968	3,487,283	2,800,609	686,674
1969	3,354,115	2,864,769	489,364

END USE (%)	1954	1964	1969
Fertilizer	80.0	57.5	54.3
Textiles	9.5	9.9	7.1
Metallurgical	1.7	2.8	2.5
Other	8.8	29.8	36.1

TRADE, metric tons	IMPORTS	EXPORTS
1967	4,526	143,037
1968	10,644	123,024
1969	14,532	114,229

TABLE 10 : JAPANESE SULFURIC ACID CONSUMPTION BY END USES (1000 metric tons)(98)

USE	1971	% change over 1970		1970
Fertilizer, total	2,330	1.1		
Ammonium Sulfate	473	0.8	Total Production	6,925,344
High Analysis Grade	1,471	3.3	Total Sales	4,843,272
Calcium Superphosphate	266	-10.8		
Dicalcium superphosphate	65	3.1		
Double burnt phosphate	55	12.2		
Industrial, Total	4,420	-2.8		
Chemical Fiber	423	-2.6		
Synthetic Fiber	600	2.5		
Titanium Dioxide	648	-3.0		
Aluminum Dioxide	207	6.1		
Sodium Bichromate	27	-		
Sodium Tripolyphosphate	285	5.9		
Hydrofluoric Acid	96	11.6		
Methacrylate Resin	214	15.8		
Others	1290	-8.2		
Grand Total	6,750	-1.5		

TABLE 11 : WORLD SULFURIC ACID PRICES (66°Bé)
For 10-20 tons lot parties market values (60-86)

Country	Feb./74-Oct./73		Oct./73-May/73		May/73-Aug./72	
		TL/ton		TL/ton		TL/ton
United States of America	1.67 cent/lb	516	1.58 cents/lb	488	1.58 cents/lb	488
Belgium	1.58 Francs/kg	553	1.58 Francs/kg	553	1.55 Francs/kg	536
France	0.15 Francs/kg	429	0.15 Francs/kg	429	0.15 Francs/kg	429
Germany	0.13 DM/kg	697	0.13 DM/kg	697	0.13 DM/kg	697
Holand	0.13 fl/kg	668	0.13 fl/kg	668	0.13 fl/kg	668
Italy	22 Lire/kg	484	22 Lire/kg	484	22 Lire/kg	484
United Kingdom	1.58 £/100kg	521	1.58 £/100kg	521	1.58 £/100kg	521

TABLE 12 : UNITED STATES Sulfuric Acid, Pyrites and Sulfur Prices (US $) (121, 128)

		Jan.1974	July/73-Jan/74	Jan/73-July/73
SULFURIC ACID,100 %tanks				
East Coast	per ton	35.75	35.75	33.75
Gulf Coast	per ton	32.75	32.75	30.75
West Coast	per ton	37.80	37.80	35.80
Other Area	per ton	35.90	35.90	33.90
SULFUR				
Refd.,99.8%pure,mines basis, 500 lb dms	100 lbs	6.60	6.60	6.60
Lump,200lb-bgs,mines basis	100 lbs	6.35	6.35	6.35
Rolls,150 lb-bgs,mines basis	100 lbs	6.10	6.10	6.10
Flour,light 50 lb-bgs,same basis	100 lbs	6.65-8.85	6.65-8.85	6.65-8.85
Refd,Sublimed,99.85% pure, 50 lb-bgs,mines basis	100 lbs	7.05	7.05	7.05
Crude,99.5 % pure,flour,50 lb-bgs mines basis ..	100 lbs	2.50-2.60	2.50-2.60	2.50-2.60
Crude,bright,molten,dom. ex-terminal Rotterdam	long tons	26.00-36.00	23.50-26.00	23.50-26.00
PYRITES				
Canadian,48-50% S mines ...	long ton	4.50-5.00	4.50-5.00	4.50-5.00

Notes:

a. 1 ton=2000 lbs, 1 long ton = 2200 lbs.

b. For prices of 60° and 66° Be,multiply by 0,7767 and 0.9319 respectively.For price of 20 % oleum multiply above prices by 1.045.Round to nearest 5 cent.

CHAPTER 2

PRODUCTION AND TRADE OF SULFURIC ACID IN TURKEY

The production of sulfuric acid in Turkey has followed a parallel pattern to the production of phosphate fertilizers. Many of the acid plants are near fertilizer plants and sell the acid to chemicals industries only when the fertilizer plants are idle due to lack of phosphate rock or others, or they decrease the production as well.

Few of the plants are associated with copper smelters and the rest are independent establishments and supply the acid to chemicals industries.

Imports of sulfuric acid are continuing, for the fertilizer sector sulfuric acid is exempt of custom duty.

Gübre Fabrikaları A.Ş. has imported phosphoric acid for triple superphosphate production substituting phosphoric acid in place of sulfuric acid, therefore its imports are included into the chapter.

CONSUMPTION BY END USES IN TURKEY

In 1970 the total production of sulfuric acid was 106,854 tons (Table 19); of which 65,028 tons in fertilizers (61.7 %), 41,826 tons outside fertilizers (39.2 %).

Table 13 showing the consumption of sulfuric acid in Istanbul Regions is a typical guide for distribution by end uses.

TABLE 13 : Consumption of Sulfuric Acid in Turkey by End Uses, 1970. (1,3,8,49,50,57,58,90, 113,116,130,147,151,152)

Sub-Sector	Sulfuric acid consumed ton/yr.	% of (total-Fertilizer ind.)	% of Total
Food	420	1.01	0.40
Textile	730	1.75	0.70
Iron and Steel	2,010	4.80	1.88
Metal working	420	1.00	0.04
Electrical appliances	740	1.77	0.70
Nonferrous metals	400	0.95	0.37
Chemicals(detergents and dyes included)	34,350	82.00	32.20
Skin and hides	2,370	5.67	2.22
Ore extraction	390	0.94	0.37
Total	41,826	100.00	
Fertilizers	65,028		61.70
Total	106,854		100.00

TABLE 14 : SULFURIC ACID DEMAND IN 1974 By USERS IN TURKEY (based on nominal capacities of such industries) (53,89,111,140,146,148)

User	Capacity in 1974 tons/yr	1974 requirement of sulfuric acid (100%) tons	
1. Ammonium sulfate			
-Karabük plant	8,000x0.742	5,940	
-Kütahya plant	80,000x0.03	2,400	
2. Normal superphosphate			
-Karabük plant	3,000		
-Elazığ plant	220,000		
-Yarımca plant	120,000		
	343,000x0.367	125,740	
3. Triplesuperphosphate			
-İskenderun plant	200,000		
-Samsun plant	220,000		
	420,000x1.045	438,900	
4. Diammoniumphosphate			
-Mersin plant	148,500x1.465	217,550	
Total in fertilizer production		790,530	88.26%
5. Aluminum sulfate (paper industry)	12,500x0.90	11,250	
6. Boric acid from colemanite	25,000x0.88	22,100	
7. Rayon	650x1.30	845	

8. Viscose	(12,000+9,050)x0.05	1,050	
9. Cellophane	(600+260)x1.750	1,490	
10.DDT	3,000x1.6	4,800	
11.Copper sulfate	2,200x1.6	3,520	
12.Explosives		10,000	
13.Iron and steel pickling			
-Ereğli plant		11,500	
-MKE plant		600	
-Karabük plant		9,000	
14.Dodecylbenzene sulfonate	10,000x0.4	4,000	
15.Other uses not specified (refineries, sodium dichromate, lead storage batteries, etc.)		25,000	
Total (outside fertilizer industry)		105,145	11.74%
Grand total		895,675	100 %

TABLE 16 : COST OF DOMESTICALLY PRODUCED SULFURIC ACIDS (TL/ton)
(5,4,8,58,111,113,116,147)

	1968	1969	1970	1971	1972	1973	1974
Murgul (85-88 %)							
Sales prices	237.50	237.50	237.50				500
Elmadağ							
105 % sales price	850	850	1050	1300	1300		1760
95 % sales price	700	700	900	950	950		800
93 % sales price	1150	1150	1150	1400	1400		1700
Koruma Tarım							
105.5 % sales price				1176	1176	1164	
98.5 % sales price	1250	1500	1500	1167	1415	1069	
95 % sales price				955	1069	873	
Karabük							
60°Bé sales price	600	600	800	800	800	800	
66°Bé sales price						900	
Benzo Kimya							
95 % production cost				620	635		900
Samsun (Azot)							
96 % production cost				650	405	440	
Bandırma							
92.5 % sales price						454	520

TABLE 18: SULFURIC ACID IMPORT PRICES REALIZED (49)
(CIF, US $)

	$ /ton
1967	26
1968	25
1969	24
1970	28
1971	29
1972	23
1973	34

TABLE 19 : CONSUMPTION OF SULFURIC ACID FERTILIZER INDUSTRY DURING 1945-1973 (91,111,141)

(tons)

PLANTS	Start-up year	Fertilizer to H_2SO_4 conversion factor	1945	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	1973
AKDENİZ GÜBRE SANAYİİ															
DAP	1972	1.465	-	-	-	-	-	-	-	-	-	-	-	3,750	6,290
T.DEMİR - ÇELİK İŞL.															
A.S (21 % N)	1945	0.742	2,968	3,430	3,710	5,194	5,194	4,766	3,636	2,895	5,216	5,072	5,343	4,766	2,659
NSP	1945	0.440	1,320	1,320	1,320	1,760	2,640	2,146	3,168	1,611	572	711	1,353	1,251	953
GÜBRE FABRİKALARI A.Ş.															
Yarımca NSP	1963	0.370	-	-	65,490	56,240	80,636	80,503	39,000	48,847	34,860	44,217	44,508	60,063	48,100
İskenderun TSP	1963	1.045	-	-	-	-	-	-	93,800 (NSP)	(a)	-	-	-	-	-
AZOT SANAYII T.A.Ş.															
Kütahya A.S (21 % N)	1963	0.003	-	-	240	255	258	258	259	235	252	241	228	232	184
Samsun TSP	1971	1.045	-	-	-	-	-	-	-	-	-	14,787	82,764	114,342	73,500
Elazığ NSP	1971	0.367	-	-	-	-	-	-	-	-	-	-	2,165	5,290	5,740
BAGFAŞ															
(NSP)	1973	0.370	-	-	-	-	-	-	-	-	-	-	-	-	14,055
Total Sulfuric Acid Consumed In Fertilizer Industry			4,288	4,750	70,760	63,449	88,728	87,673	80,769	53,588	40,900	65,028	136,361	189,694	151,481
Total Sulfuric Acid Consumption (Production+import)			11,319	37,591	86,051	66,693	107,013	114,773	110,008	102,531	81,332	106,854	173,322	272,716	251,096
Consumption Of Sulfuric Acid Outside The Fertilizer Industry			7,031	32,841	15,291	3,244	18,285	27,100	29,239	48,943	40,432	41,826	36,961	93,022	99,615

(a) : For TSP production the Firm has imported phosphoric acid instead of sulfuric acid.

TABLE 21 : IMPORT OF PHOSPHORIC ACID (157, 158, 159, 160)

Tariff and Statistical No:	1967	1968	1969	1970	1971	1972	1973
28.10.20 Phosphoric Acids	129,659 kg	27.305.369	45.062,455	14.104,661	52.565.639	67,543.419	52.008.020
	302,808 TL	20.817,677	34.051.664	10.808.488	48,341,897	63,237,931	68,469.157
	2335TL/ton	762 TL/ton	755 TL/ton	766 TL/ton	917 TL/ton	936 TL/ton	1516 TL/ton
	257 $/ton	85 $/ton	83 $/ton	84 $/ton	61 $/ton	67 $/ton	94 TL/ton
				26.472.241			
				29,451.793			
				1112 TL/ton			
				73 $/ton			
Total				40,576,902			
Amount of Phosphoric acid imported by GÜBRE FABRİKALARI A.Ş. (50 %) (tons)		37.145	37,383	47,607	53.896	67,827	

1 ton of TSP requires 0.324 ton 100 % phosphoric acid or 0.648 ton 50 % phosphoric acid.

CHAPTER 3

CONSUMPTION TRENDS

The purpose of this study is to find out the sulfuric acid demand of Turkey which has an ever-changing economic and agricultural character.

The greatest demand for sulfuric acid is in fertilizer industry, almost 85-90 %, as it is the case in most of the developing countries.(Tables, 6, 7, 9, 10, 13) The selling prices of fertilizers are determined by the Government and most of the acid factories are built in parallel to the fertilizer plants in a nearby location. The transportation of sulfuric acid is difficult so the demand is not very elastic.

According to the Third Five Year Development Plan targets, fertilizer demand will be met by the indigenous production mainly, 23 % of the demand for nitrogenous fertilizers and 24 % of phosphate fertilizers are supplied by native fertilizer plants.

Obviously, it is impractical to produce all the fertilizers within the country, so the imports will continue during the Third Plan period. It is also the aim of Third Five Year Development Plan to increase the production of the nitrogenous fertilizers by 32 % per year, and the phosphate fertilizers by 24 % per year.

The actual fertiliser production figures are shown in Table 15 and Figure 2.

The remaining part of sulfuric acid produced is used in various chemicals industries, this part constitutes almost 10-15 % of total demand.

At the beginning of planned periods the chemicals industries production was limited to few consumption goods, whereas the intermediates production started to replace them. During the first and second plan periods the increase in annual production was 16.6 % on the average. In this sector the Third Five Year Development Plan forecasts:

a. 13.4 % annual increase in production
b. establishment of competitive plants with optimum capacity in order to decrease imports to minimum.
c. providing export facilities
d. increasing the production of export-oriented products.

To approximate the consumption of sulfuric acid in Turkey with the above information, three approaches have been considered.

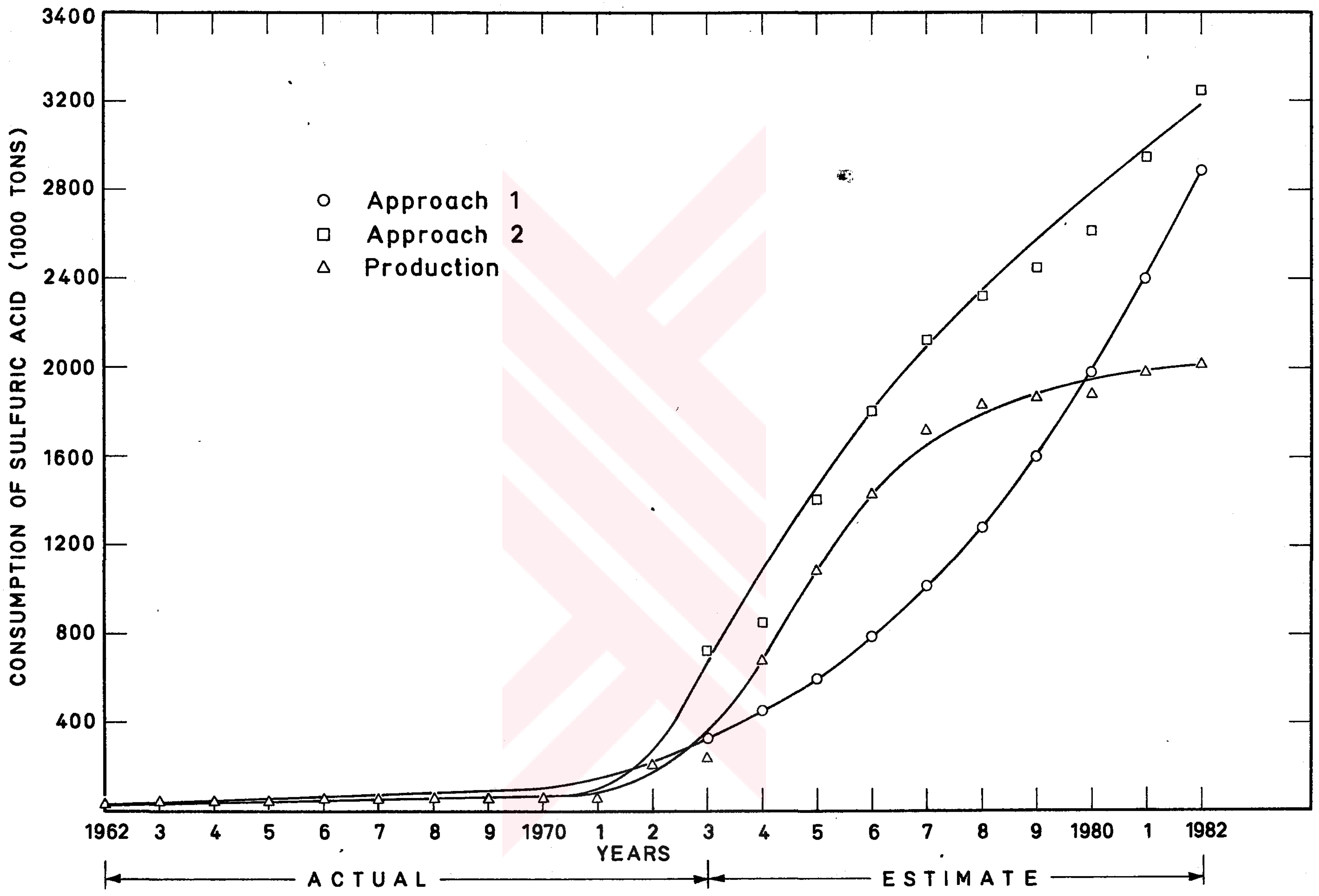

FIGURE 1: Consumption Trends of Sulfuric Acid in TURKEY.

3.1. Approach 1 :

In the first approach, the total demand for sulfuric acid is considered to be composed of fertilizer and chemicals industries requirements.

The demand for sulfuric acid in fertilizer industries is taken from Table 20, as the requirement of existing and projected phosphatic fertilizer plants.

The sulfuric acid requirement in chemicals industries is evaluated increasing the 1974 demand from Table 14 by 13.4 % annual rate of increase suggested by the Third Five Year Development Plan, for chemicals production.

TABLE 22 : Demand for Sulfuric acid–approach 1 (1000 tons)

Year	Demand in chemicals industries	Demand in fertilizer industries	Total
1973	91	626	717
1974	105	745	850
1975	141	1,267	1,408
1976	189	1,608	1,797
1977	253	1,879	2,132
1978	339	1,978	2,317
1979	454	2,002	2,457
1980	609	2,012	2,621
1981	316	2,123	2,944
1982	1,093	2,154	3,247

3.2. Approach 2:

In the second approach, the consumption is evaluated by an econometric analysis, where the selection of variables affecting the consumption is important.

In this analysis, it is estimated that the predominating variable on sulfuric acid demand is the production of fertilizers using sulfuric acid, therefore the consumption of sulfuric acid in fertilizer manufacture (Table 19) is the number 1 independent variable (X_1).

The second independent variable (X_2) affecting the sulfuric acid consumption is chosen as the chemicals industries production, which consumes the remainder of sulfuric acid outside the fertilizer industry. (Table 23)

In this analysis, the trend equation for sulfuric acid consumption (dependent variable Y) is calculated by the computer regression analyses in two models:

a. for linear relation : $Y = a_o+a_1X_1+a_2X_2$

b. for exponential relation: $Y=e^bX_1^{C_1}X_2^{C_2}$ or

$$\ln Y = b+c_1\ln X_1+c_2\ln X_2$$

The constants are calculated as:

a. $Y = 27.95600+0.03978X_1+0.03632X_2$

b. $Y = e^{0.95797}\ X_1^{0.33863}\ X_2^{0.21576}$

These are the equations based on the past data of

X_1, X_2 and Y. In order to project sulfuric acid consumption figures, the projections of independent variables are done by finding their respective best fitting curve equations through method of least squares. (Fig.2A,2B)

The equations so found for X_1 and X_2 are:

$$X_1=2821.07-324.46\,x - 43.249\,x^2 + 15.862\,x^3$$

$$X_2= 195.3622+158.5695x + 33.7771\,x^2$$

where x refers to years starting from 1967.
These equations are projected by increasing the x values for future; then the projected X_1 and X_2 values are substituted in Y equation for the same year, and sulfuric acid consumption estimates are so calculated.

The comparison of the two models in Table 26 show that the single and multiple correlation coefficients between dependent and independent variables are higher in linear model, sum of squares of residuals is almost half that of exponential model; standard error of estimate is a bit greater in linear model (Table 25). The sulfuric acid requirement of present, on- erection and projected fertilizer plants (Table 20) is much above exponential model results, but close to linear one. Therefore, linear model is chosen as the best fitting equation and projection figures for sulfuric acid consumption are more real.

TABLE 23 : TOTAL CHEMICAL INDUSTRIES PRODUCTION

(Input Data for Variable X_2)(85,86,122)

Years	Production Value (million TL. based on current prices)	Wholesale prices for chemicals and pharmaceuticals		Production value (deflated)	Index value
		1963=100	1962=100	1962=100	1962=100
1962	1268	97.2	100.0	1268	100.00
1963	1330	100.0	102.8	1367	107.80
1964	1415	102.0	104.9	1484	117.03
1965	1470	111.0	114.1	1677	132.25
1966	1840 (x)	129.8	133.5	2456	193.69
1967	2366	140.0	144.0	3407	268.69
1968	2779	140.8	144.8	4024	317.35
1969	3675	143.1	147.2	5410	426.65
1970	4594	202.4	208.2	9565	754.33
1971	5580	327.8	337.2	18816	1483.91
1972	6993	346.0	355.9	24888	1962.77

(x) : interpolated

TABLE 24 : INPUT DATA FOR ECONOMETRIC TREND ANALYSIS

years	Y, total sulfuric acid consumption, tons, Table 15	X_1, sulfuric acid consumption in fertiliser production tons, Table 15	X_2, total production in chemicals industries million TL	X_1 index	X_2 index
1962	37,591	4,750	1,268	100.00	100.00
1963	86,051	70,760	1,367	1489.68	107.80
1964	66,693	63,449	1,484	1335.76	117.03
1965	107,013	88,728	1,677	1867.95	132.25
1966	114,773	87,675	2,456	1845.74	193.69
1967	110,008	80,769	3,407	1700.40	268.69
1968	102,531	53,588	4,024	1128.16	317.35
1969	81,352	40,900	5,410	861.05	426.65
1970	106,854	65,028	9,565	1369.01	754.33
1971	173,322	136,361	18,816	2870.75	1483.91
1972	272,716	189,694	24,888	3993.55	1962.77

TABLE 25 : OUTPUT OF ECONOMETRIC ANALYSES

	Correlation coef. between X_1 and Y	Correlation coef. between X_2 and Y	Multiple correlation coef. between Y, X_1 and X_2	Standard error of estimate	Sum of squares of residuals
Case 1 : Linear analysis	0.95868	0.90917	0.98023	13.79217	1522.3735
Case 2 : Exponential analysis	0.88495	0.79962	0.96240	(ln a 0.15274) 1.1648	3878.7267

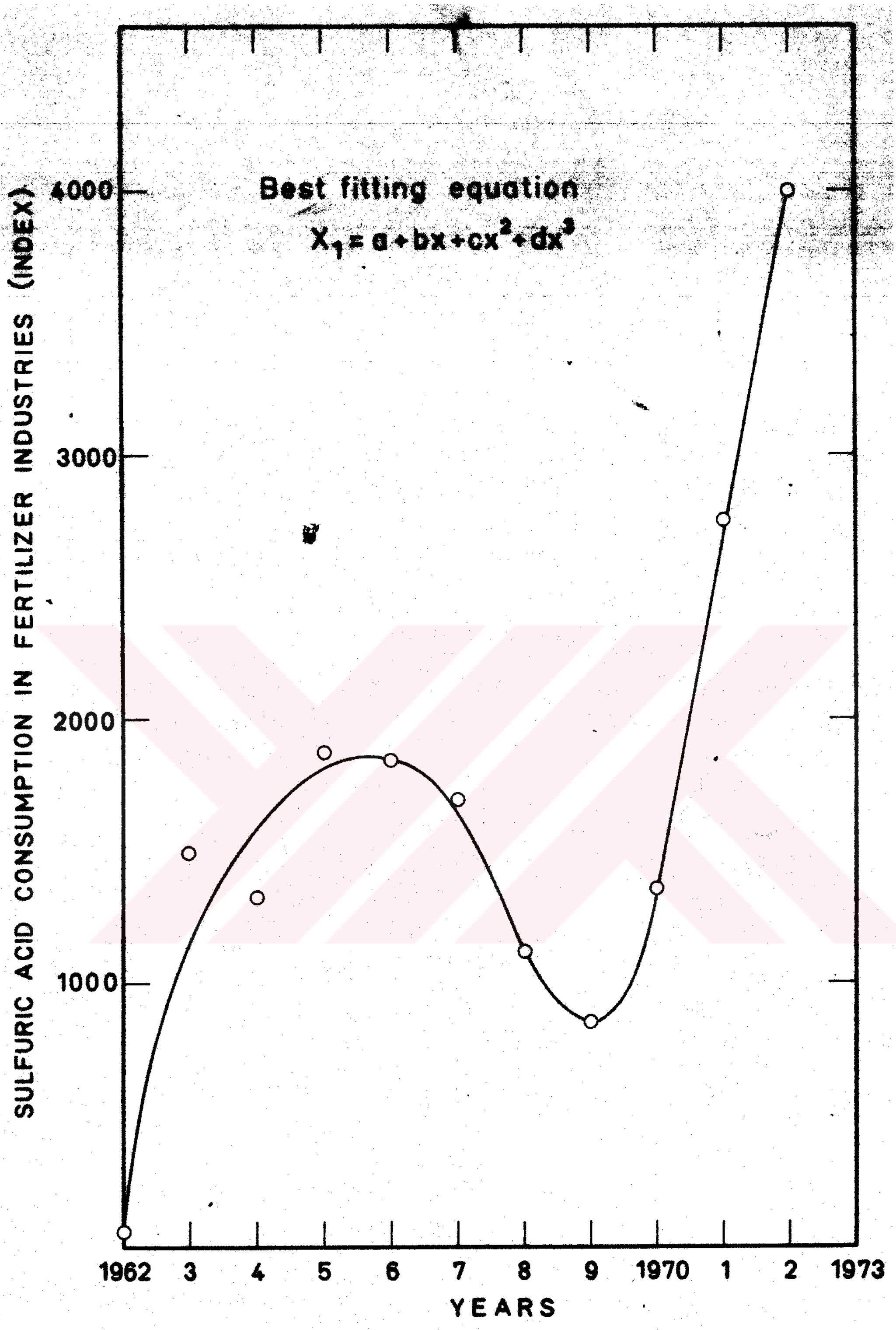

FIGURE 2A: Phosphatic Fertilizer Plants Sulfuric Acid Consumption.

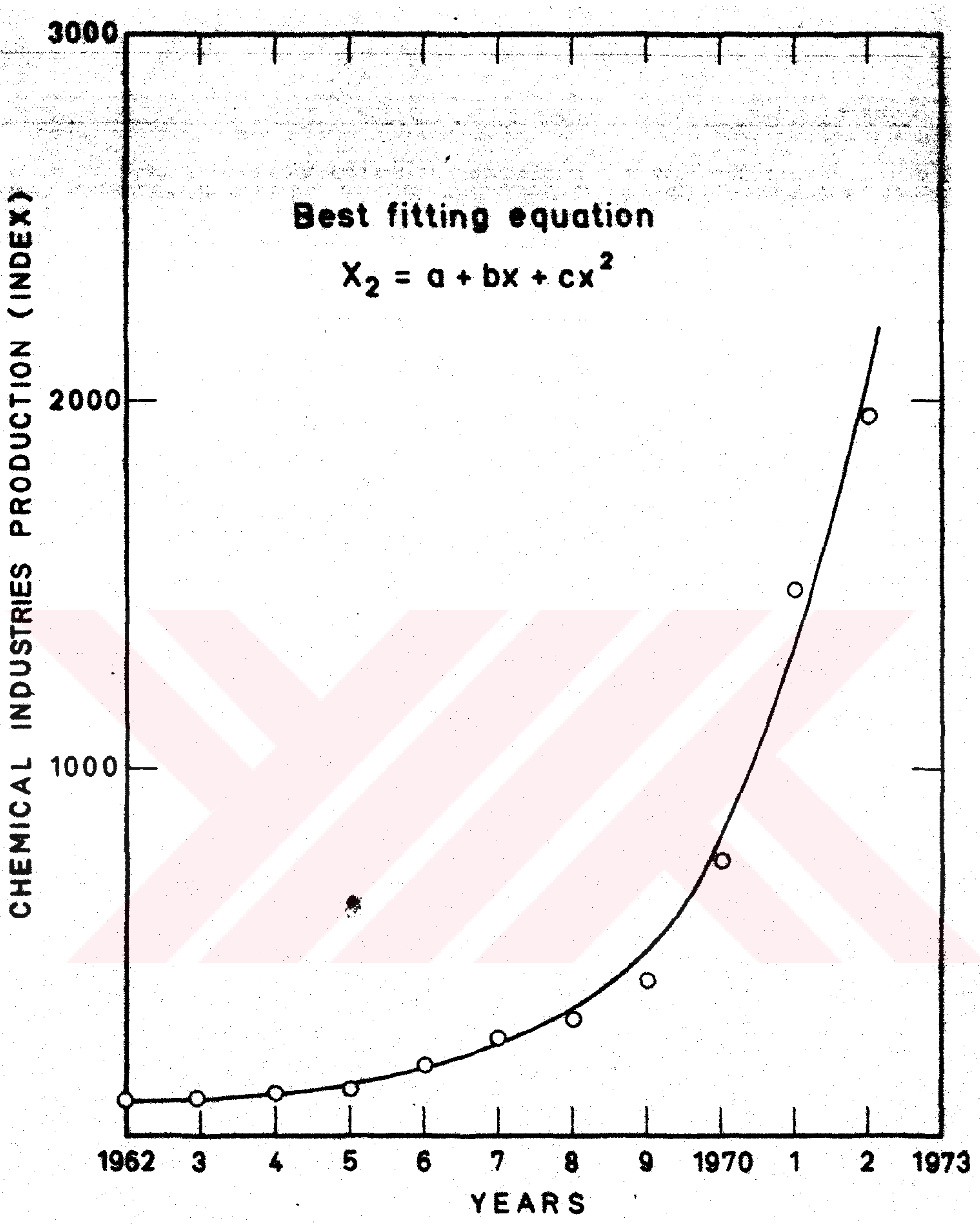

FIGURE 2B: Total Value of Chemical Industries Production.

TABLE 26 : SULFURIC ACID DEMAND ESTIMATION BY APPROACH 2 (1000 tons)

Years	Linear model	Exponential model
1973	336	259
1974	452	305
1975	602	364
1976	788	414
1977	1,015	473
1978	1,287	537
1979	1,607	597
1980	1,978	661
1981	2,406	733
1982	2,893	859

3.3. Approach 3:

This is the usually applied method in setting up plants and projects of sulfuric acid in Turkey.

The transportation of sulfuric acid is a real problem, especially in Turkey's conditions; because it requires special wagons, it is very difficult both in terms of carriage and traffic load in railways, and this type of supply is not continuous but in parties.

Due to transportation difficulties, sulfuric acid plants are built nearby the major consumption centres, as a tendency all over the world; in Turkey mostly near the fertilizer plants. Considering the view as such, the existing sulfuric acid plants and their end uses are noted in Table 27, which indicates that there remains only Yarımca NSP and TSP plants of Gübre Fabrikaları A.Ş.. of which sulfuric acid requirements were imported by now.

TABLE 27 : SULFURIC ACID DEMAND ESTIMATE BY APPROACH 3

Sulfuric Acid Plants	Consumption Places
Murgul	non-fertilizer industry
Ergani	Elazığ NSP Factory
Karabük	in-plant, Karabük NSP Factory
Bandırma	BAGFAŞ NSP Factory
Samsun (Azot)	in-plant
Samsun (KBİ)	Samsun DAP expansion Factory
Mersin	in-plant (Akdeniz DAP Factory)
İskenderun	in-plant
Elmadağ	explosives, accumulator and non-fertilizer industry
Derince	non-fertilizer industry
Hasanoğlan	non-fertilizer industry
Arılar	non-fertilizer industry

TABLE 28 : DEFICIT OR SURPLUS IN PRODUCTION OF SULFURIC ACID BY THREE APPROACHES

Years	Approach 1	Approach 2	Approach 3
1973	480 deficit	98 deficit	YARIMCA TSP plant's annual surfuric acid requirement is 209,000tons which is the only plant not having a sulfuric acid unit
1974	134 deficit	234 surplus	
1975	316 deficit	490 surplus	
1976	360 deficit	648 surplus	
1977	412 deficit	705 surplus	
1978	482 deficit	548 surplus	
1979	597 deficit	253 surplus	
1980	752 deficit	109 surplus	
1981	959 deficit	421 deficit	
1982	1,236 deficit	882 deficit	

3.4. Comparison of the three approaches (Table 28):

a. The first approach gives a rough indication of deficit. In evaluating these figures, the basic assumptions made are:

- the phosphatic fertilizer plants operate at full capacity,

- the chemical industries need sulfuric acid at an increasing annual rate of 13.4 % as denoted by the Third Five Year Development Plan.

First assumption is very rough, because all phosphatic fertilizer plants are deeply in need of phosphate rock, some of them ammonia; which create important bottle-necks being import-oriented.

Whereas the goal of 13.4 % annual increase in production in chemicals industries is realized in 1973 program as 14.1 %. However, fertilizer sector dominates in consumption of sulfuric acid.

b. The second approach is an econometric analysis taking into account all major effects related to sulfuric acid consumption. The actual consumption and production figures are taken as the bases and expected values are calculated following the same pattern.

The sulfuric acid production for 1973 was expected to be 597,000 tons, but it is realized as 237,000 tons with only 6,200 tons of import. Whereas, approach 1 indicated a deficit of 480,000 tons, approach 2

98,000 tons. This means that the second approach is more reliable.

c. In the usual way of establishing sulfuric acid plants, almost all sulfuric acid plants correspond to some fertilizer plants; in this respect there remains only Yarimca Fertilizer Plant without a sulfuric acid unit.

As a conclusion, it can be stated that approach 1 shows the upper limit, approach 3 the lower limit of deficit in production; and approach 2 is found more reliable, therefore it is accepted as the basis for capacity selection suggestions in conclusion.

CHAPTER 4

RAW MATERIALS

4.1. Raw Material Situation in the World:

The sulfuric acid industry, although one of the oldest branches of the chemical industry, continued to expand at a rapid rate during the sixties and new plants were put on stream every year in the various regions of the world. Indeed sulfuric acid continued to be the most common and most used of the main industrial acids despite the periodic fluctuations which occurred in the supply of its raw materials (82-85,114).

With regard to raw materials, two periods could be noted during the last ten years. At the beginning of the 1960's all European producers suffered from a serious shortage of raw materials which resulted in a considerable increase in prices and in a consequent decline in the activity of a number of producers. This situation changed from 1965 onwards because of the increase in deliveries of recovered sulfur from France and of massive exposts of brimstone from Poland.

However, sulphurous products are very complementary and in the case of shortage or over-supply of one product, the production of another can be increased or diminished to maintain the balance of supply and demand.

Among the sulphurous materials brimstone and pyrites accounted for the largest proportion, although the production of sulfur in forms such as other sulfides, gypsum and anhydrite, is fast increasing and the annual rate of expansion is higher than that of pyrites.

4.1.1. Production :

The world production of sulfur in all forms amounted in 1969 to about 39 million tons, including 21 million tons of brimstone, 11 million tons of sulfur in pyrites and about 7 million tons of sulfur in other forms. The largest producers of brimstone were the United States (about 9 million tons), Canada (about 4 million tons) and Poland (about 2 million tons) and of pyrites the USSR (about 3 million tons), Japan (1.4 million tons) and Spain (1.3 million tons).

Among the largest producers (Table 30), USA, USSR, Poland, France and Finland export a large part of their production. The other countries including Italy, the UK and the Federal Republic of Germany, which produce significant quantities of sulfurous material depended largely on imports for their production of sulfuric acid. (49)

The kind of raw material used for the manufacture of sulfuric acid varies from country to country, depending for producing countries on the material available and for the non-producing countries, on the conditions of supply on the international market.

In the United States the raw material structure of the sulfuric acid industry differs from that of European acid production. More than 80 % of sulfuric acid in the United States was derived from brimstone whereas in Europe the proportion was around 50 % (Table 29). Indeed, in Europe the role of pyrites continued to be important, notably for the pyrites-producing countries such as Sweden, Portugal, Spain, the USSR, Italy and Western Germany, For these countries pyrites remained attractive, on the one hand because of their relatively low and stable cost and on the other because of the ferrous and non-ferrous components of the residues which can be otherwise utilized.

However, since 1965 recovered sulfur and brimstone have gained in importance in the European sulfur market, due to the considerable increases of production of recovered sulfur in France and of brimstone has become very large and has been in excess of demand since 1968. Consequently the price was significantly reduced making brimstone very competitive with the other sulfurous materials including pyrites. And, although pyrites still hold a prominent position in Europe, this situation has already caused the replacement of several pyrites-based plants nearing obsolescence by newer brimstone-based installations.

The world export of brimstone reached in 1970 the figure of 8 million tons. Canada, Poland, USA, France and Mexico belong to the group of chief brimstone exporters in the world and their total export accounts for 91 % of the present overall export. (Table 30)

TABLE 29 : RAW MATERIALS USED IN THE MANUFACTURE OF SULFURIC ACID, IN VARIOUS COUNTRIES; 1968 (61) (in percentages)

COUNTRY	SULFUR	PYRITES	OTHER SULFIDES	ANHYDRITE GYPSUM	PURIFICATION MASSES
Belgium	39	31	30	-	-
Federal Rep.of Germany	17	65	18	-	-
France	70	15	14 (including H_2S)	-	1
Hungary	55				
Italy	8	86	5	-	1
Netherlands	56	9	8	23	4
Poland	83	12	-	5	-
Spain	-	97	3	-	-
United States	80	6	5	-	9
Japan	-	67	33	-	-
Sweden		almost 100			

TABLE 30 : WORLD BRIMSTONE EXPORTERS (114)

Year	USA	Mexico	France	Canada	Poland	Total %
1954	100.0	–	–	–	–	100.0
1955	90.0	10.0	–	–	–	100.0
1960	50.0	34.7	11.7	3.6	–	100.0
1965	39.8	22.9	13.6	20.2	3.5	100.0
1970	18.0	8.9	15.2	34.0	23.9	100.0

4.1.2. Consumption :

In forecasting the development of sulfur demand, it will be possible to rely mainly on the predictable development of requirements and on the production development of sulfuric acid and phosphatic fertilizers.

Over a long period of time, however, the average index of production of phosphatic fertilizers was about 8 % per annum.

Similar was the case of sulfuric acid whose production was at the average index growth per annum of about 7.5 %, with the very low growth index of about 4 % in 1967.

Taking into account the fact that the industries of fertilizers and sulfuric acid are the biggest consumers and knowing the average rate of growth, volume of expected sulfur consumption in 1975 and 1980 was deducted.

It is a well-known fact that the growth of annual rate of sulfur consumption in other industries apart from the fertilizer sector, is somewhat lower, within approximately 5 %.

On the whole, it seems that it would be unrealistic to adopt the future consumption growth index for sulfur in all forms at the rate of 7-8 % and therefore an annual average index of about 6 % should rather be adopted.

The growth of consumption of brimstone is estimated at about 7 % in the market-economy countries and at about 10 % in the centrally planned-economy countries in connection with a more intensive development of fertilizer production there while the growth of pyrites will be about 1 % or less each year (Table 30).

In 1980 the world production of phosphate fertilizers will reach the maximum of 35 million tons of P_2O_5. If the production of sulfuric acid increases by the same percentage it will account for approximately 160 million tons by 1980. To secure that production level, it will be necessary to have about 53.5 million tons of sulfur. Assuming that the amount of sulfur required for the production of sulfuric acid accounts for about 80 % of the total use of sulfur, the estimate of sulfur needs in all forms and in terms of all directions in 1980 will close with the figure of about 67 million tons, thus almost identical with that calculated on the basis of the growth index of consumption.

TABLE 51 : WORLD DEMAND FOR SULFUR IN 1975-1980 (million tons)(114)

Year	World demand for sulfur in all forms	Including			Total demand for sulfur in all forms in market-economy countries	Including		
		brimstone	pyrite	other sources		brimstone	pyrite	other sources
1975	49.4	29.9	11.8	7.7	38.8	24.5	7.9	6.4
1980	67.7	45.0	12.3	10.4	50.6	34.3	8.3	7.8

4.1.3. Supply Forecast :

In summary, production in million tons would be as:

		1975		1980
Brimstone		31.7	about	45.1
Pyrites	about	12.0	about	12.0
Other sources	about	8.0	about	11.0
		51.7		68.1

Here, the basic assumptions made are as follows:

It seems that in connection with the present situation, conditioned by big supplies of brimstone and its low prices, it may be assumed that in the coming years the production of pyrites will show an insignificant growth to meet but the own increase in demand in the countries which produce that raw material or that the production of pyrites may show a stagnant tendency in view of lower needs in importing countries.

As regards the sulfur obtained from the other sources, it is extremely difficult to evaluate its growth. It seems that the growth of sulfur from the world metallurgical operations may be estimated at 2-2.5 million tons, on an average, between 1970 and 1975 up to about 8 million tons and by some 2.5-3 million tons upto about 11 million tons in the next years.

In connection with the big demand for gas as a source of power, its production and the growth of sulfur thus recovered as a by-product will be on increase.

4.1.4. Price Forecast :

It is a fact that demand for brimstone will be increasing as a result of the development in fertilizers and other industries that need this raw material. At the current supply figures well exceeding demand and low prices, the growth of new productive capacities will be based mainly on brimstone.

It is also obvious that the fatal sulfur is unable to meet full demand for sulfur and that the producers of mined sulfur or that obtained by an underground melting process bears its full production costs. Thus, a further drop in prices which are on the borderline of production costs would in consequence force those producers to limit or stop their production, which action would involve a shortage of sulfur and increased prices. Bearing these aspects in mind, it seems that further decline in prices which have already reached their lowest level would be impossible. Neither should one expect too high prices and high cyclic fluctuations similar to those in the past, for new factors such as the air pollution legislation, the existence of fatal sulfur etc., which were of no bearing in the past, will be influential.

On account of the production costs of sulfur, it should rather be expected that over the coming decade only a moderate increase in sulfur prices could take place, depending on the quantity of the respective lot, kind of sulfur and export designation.

TABLE 32 : World Prices per ton of Brimstone (FOB-US $)
(111,121-128, 166)

Years	$/ton
1954	30
1955	30
1956	28
1957	27
1958	25
1959	24
1960	23
1961	22
1962	22
1963	20
1964	20
1965	24
1966	30
1967	39
1968	41
1969	37
1970	18
1973	23.5

TABLE 33 : PRODUCTION, TRADE AND CONSUMPTION BY THE CHEMICAL INDUSTRY OF SULFUR AS SUCH IN EUROPE, THE UNITED STATES OF AMERICA AND JAPAN IN 1969, 1970 AND 1971 (137,154)

(tons of S)

COUNTRIES	PRODUCTION			IMPORTS			EXPORTS			Consumption by the Chemical Industry		
	1969	1970	1971	1969	1970	1971	1969	1970	1971	1969	1970	1971
Austria	–	–	3,000	2,481	2,187	5,745	–	–	–	39,571	60,478	–
Belgium	10,000	14,000	23,000	303,200	331,300	425,600	500	300	500	292,200	297,000	436,000
Bulgaria	5,300	5,463	5,773	–	–	–	16,321	11,098	14,639	–	–	–
Czechoslavakia	7,000	7,000	5,000	267,000	303,000	279,000	–	–	–	–	–	–
Chile	99,000	109,000	–	–	–	–	–	–	–	–	–	–
Denmark	7,128	8,240	5,185	11,632	11,142	15,308	144	44	7	18,616	19,338	20,486
Fed. Rep. of Germany	129,000	176,000	184,000	321,000	292,000	332,000	36,000	34,000	44,000	445,000	–	–
Finland	112,000	115,000	101,000	35,000	–	53,000	–	12,000	–	147,000	103,000	154,000
France	1,697,000	1,733,000	1,812,000	–	–	428,000	–	–	948,000	–	–	–
German Dem. Rep.	109,554	109,022	99,915	–	–	–	–	–	–	–	–	–
Greece	–	–	–	–	–	–	–	–	–	–	–	–
Hungary	2,526	3,223	3,290	95,094	118,021	110,327	–	–	–	106,340	110,972	115,121
Italy	–	151,000	134,000	–	301,000	284,000	–	6,000	4,000	–	446,000	414,000
Mexico	1,716,000	1,381,000	1,178,000	–	–	–	–	–	–	–	–	–
Netherlans	31,000	33,200	33,500	389,400	416,200	441,600	1,400	900	200	–	–	–
Norway	–	–	–	33,931	33,586	21,146	18	5	–	–	–	–
Poland	1,942,000	2,683,000	2,711,200	–	–	–	1,449,612	1,773,000	2,064,000	347,800	468,600	597,598
Portugal	3,815	3,148	2,384	–	–	–	–	–	–	–	–	–
Spain	34,049	35,980	42,334	75,682	68,245	81,946	358	530	175	26,500	33,000	35,000
Switzerland	–	–	–	55,000	65,000	51,000	–	–	–	54,000	55,000	51,000
Turkey	25,700	26,760	23,650	–	–	–	–	–	–	–	–	–
USSR	–	1,120,000	–	–	–	–	–	–	–	–	–	–
United Kingdom	43,200	36,700	25,800	739,800	814,600	961,500	2,100	2,200	2,200	662,900	714,700	805,000
Yugoslavia	–	–	–	21,205	20,590	20,377	–	–	2,265	9,128	7,041	1,779
United States	8,697,000	8,667,000	8,749,000	1,703,000	1,562,000	1,318,000	1,575,000	1,456,000	1,557,000	8,203,000	8,114,000	8,229,000
Japan	299,000	146,000	96,000	–	–	–	–	–	–	–	–	–

TABLE 34 : PRODUCTION, TRADE AND CONSUMPTION BY THE CHEMICAL INDUSTRY, OF PYRITES AND OTHER SULFIDES, IN EUROPE, THE UNITED STATES OF AMERICA AND YAPAN IN 1969, 1970 AND 1971 (135)

(tons of S)

COUNTRY	PRODUCTION			IMPORTS			EXPORTS			CONSUMPTION BY THE CHEMICAL INDUSTRY		
	1969	1970	1971	1969	1970	1971	1969	1970	1971	1969	1970	1971
Austria	386,000	-	-	248,772	257,362	291,095	2,288	-	-	-	-	-
Belgium	-	-	-	357,100	393,700	319,500	17,800	62,800	7,300	364,200	346,800	317,600
Bulgaria	68,000	-	-	-	-	-	-	-	-	-	-	-
Czechoslavakia	136,000	-	-	33,000	76,000	58,000	-	-	-	-	-	-
Denmark	-	-	-	174,182	187,127	187,798	146,113	133,110	112,953	28,069	54,017	74,845
Fed. Rep. of Germany	345,000	323,000	308,000	1,023,000	958,000	-	17,000	13,000	14,000	1,291,000	1,326,000	-
Finland	375,000	213,000	198,000	-	-	-	-	-	-	-	213,000	198,000
France	32,000	-	49,000	-	-	215,000	-	-	-	-	-	-
German Dem. Rep.	58,000	-	-	108,478	106,582	74,433	-	-	-	-	-	-
Greece	114,000	-	-	-	-	-	-	-	-	-	-	-
Hungary	-	-	-	56,128	49,221	49,025	-	-	1,931	52,267	48,593	46,397
Ireland	-	-	-	-	-	-	-	-	-	-	-	-
Italy	649,000	707,000	706,000	-	417,000	283,000	-	14,000	17,000	-	1,110,000	860,000
Netherlands	3,300	1,200	-	59,900	70,300	64,000	-	-	-	69,700	69,100	63,800
Norway	352,000	339,650	-	-	-	-	503,803	520,799	545,236	-	-	-
Poland	96,417	34,382	-	-	-	2,107	-	-	-	364,800	354,100	10,636
Portugal	235,288	212,693	294,093	-	-	-	-	-	-	-	-	-
Romania	287,000	-	-	-	-	-	-	-	-	-	-	-
Spain	1,251,095	1,394,621	1,468,700	47	38	32	481,483	415,973	440,273	960,000	958,600	996,900
Sweden	250,000	-	-	-	-	-	-	-	-	-	-	-
Switzerland	-	-	-	14,000	8,000	11,000	-	-	-	14,000	8,000	11,000
Turkey	129,844	91,108	58,447	-	-	-	-	-	-	-	-	-
USSR	1,850,000	-	-	-	-	-	-	-	-	-	-	-
United Kingdom	-	-	-	197,300	163,900	182,400	-	-	-	210,500	202,800	182,900
Yugoslavia	163,471	195,195	160,697	19,600	36,461	71,987	49,197	23,190	35,273	133,306	152,900	196,350
United States	360,000	-	-	132,000	132,000	100,000	-	-	-	1,097,000	1,148,000	1,090,000
Japan	1,886,000	-	-	-	-	-	-	-	-	-	-	-

4.2. Raw Material Situation in Turkey (55,111,148)

Turkey disposes of a great variety of possible sources of sulfur. Main forms in which sulfur is available in Turkey are as follows:

1. brimstone (elemental sulfur)
2. pyrites (ores and concentrates), pyritic copper ores and concentrates, sulfidic zinc and lead ores and concentrates.
3. gypsum
4. petroleum and natural gas

4.2.1. Native Sulfur : Keçiborlu sulfur ores in Isparta:

The owner of the mines is Etibank. For the date 1.1.1974, the occurences are (58)

visible reserves	1,300,492 tons
- ready to mine (43.3 % S)	303,548 tons
- not ready to mine (39.5 % S)	996,944 tons
probable reserves (60.0 % S)	122,940 tons
possible reserves (32.6 % S)	230,000 tons
TOTAL	1,653,432 tons

Ores of tenor less than 41 % S are concentrated by floatation. The present sulfur-production capacity at Keçiborlu Mines is as follows :

floatation plant	20,000 tons/year
direct smelting	15,000 tons/year
Total	35,000 tons/year

4.2.2. Pyrites (pyritic copper ores and concentrates, sulfidic zinc and lead ores and concentrates)

Although Turkey has many rich pyrites deposits; due to the insufficient investigations these deposits are not used up efficiently. By now these ores are used domestically and also exported for their copper content.

4.2.2.1. Etibank Küre pyrites exploration :

This plant has been set up for the exportation of copper ores in 1955. The present capacity is 125,000 tons per year and production is mainly limited by the exports. (Table 36)

The total reserves with respect to the beginning of 1974 for 2.03 % Cu and 45.43 % S containing ores on the average is 1,309,930 tons. Existing ores can last untill 1984.

4.2.2.2. Etibank Keçiborlu Mines :

In this plant pyrites is obtained as a by-product:

a. Refinery slag (cake) : This cake is a 60 % S containing pyrites, annual production capacity is 20,000 tons.

b. Floatation residues : Residues containing 20 % S are produced 30,000 tons per year.

These two sources of sulfur will be diminished by 1982; MTA continues searching new deposits in this area.

TABLE 35 : SALES PRICES OF SULFUR IN TURKEY (50,111)
(TL/ton)

	Keçiborlu prices	Import prices
1963	497	
1964	499	
1965	500	
1966	488	
1967	368	
1968	505	
1969	680	
1970	661	
1971	680	
1972	712	
1973	1200	1850
1974	1850	1850

4.2.2.3. Etibank Ergani Floatation Pyrites Plant :

Ergani Copper Smelting Plant has the production capacity of 225,000 tons per year of floatation pyrites as a by-product. But, the sulfur content of this pyrites is rather low (42 %).

This can be used by mixing with high sulfur- content ores, obviously the usage of this product is dependent on the presence and productions of the ore. If the result of new investigations is not positive, present ores will endure by 1984.

4.2.2.4. Etibank Murgul Copper Smelting Plant, Floatation Pyrites :

Floatation plant in Murgul has the capacity of producing 35,000 tons of 40 % S pyrites per year. Considering the visible reserves, it is estimated that production will continue until 1983.

The investigations by MTA are continuing along the Black Sea Coast at various locations, mainly at Çakmakkaya, Merzifon, Bulancak and Kızılkaya.

4.2.2.5. K.D.I. Murgul Floatation Pyrites :

This plant started operation in 1973 and is supposed to produce 220,000 tons of 46 % S per year. Considering the visible reserves, production is estimated to continue till 1986, but production will drop to 180,000 tons per year in 1980.

4.2.2.6. K.B.I. Küre Mines

This plant contains 1.8 million tons visible and 2.5 million tons probable reserves of pyritic copper. It is planned to produce 180,000 ton cupric pyrites (43.5 % S) per year.

4.2.2.7. K.B.I. Espiye-Lahanos Pyrites :

Main deposits of sulfidic Pb-Zn ores are located along the Black Sea Coast. Total reserves of these ores have been estimated at about 2.3 million tons with 39.5 % S.

TABLE 36 : THE PRODUCTION AND EXPORTS FROM KÜRE MINES (50,55)

Years	Production (tons)	Exports (tons)
1965	132,100	115,000
1966	120,600	91,200
1967	125,000	119,400
1968	130,000	129,500
1969	124,400	98,000
1970	88,600	55,000
1971	58,000	44,000
1972	85,700	43,400
1973	43,500	6,200

4.2.3.1. Gypsum Deposits :

Turkey has aboundant amount of gypsum deposits of which important ones are given in Table 38. Table 37 shows the production and demand for gypsum.

4.2.3.2. By-Product Gypsum (3) :

The annual gypsum mud (gipsschlamm) out of Samsun I and II plants are :

Samsun I (TSP)	1,075,000	m^3/year
Samsun II (DAP)	1,690,000	m^3/year

containing 322,500 m^3/year and 507,000 m^3/year of solid material respectively. The solid phase analysis is as follows :

Moisture	13.000 %
Water-Soluble P_2O_5	0.027 %
Water-insoluble P_2O_5	0.065 %
CaO	33.600 %
SO_4	47.330 %
Fe_2O_3	0.120 %
SiO_2	1.240 %
Al_2O_3	0.330 %
others	3.703 %

(F is not analyzed.)

with average density : 1.47 gr/cm^3.

$CaSO_4$ output of each plant is calculated and found to be

$$322{,}500 \times 1.47 \times \frac{136}{56} \times 0.336 = 387{,}000 \text{ ton/yr.}$$

$$507{,}000 \times 1.47 \times \frac{136}{56} \times 0.336 = 608{,}000 \text{ tons/year.}$$

The other TSP and DAP plants are calculated similarly:

	Nominal Capacity	By-Product calcium sulfate
Samsun I (TSP)	220,000 tons/yr.	387,000 tons/yr
Samsun II (DAP)	139,500 tons/yr	608,000 tons/yr
Yarımca (TSP)	200,000 tons/yr	352,000 tons/yr
İskenderun (TSP)	200,000 tons/yr	352,000 tons/yr
Mersin (TSP)	148,500 tons/yr	646,000 tons/yr
Total		2,345,000 tons/yr

4.2.4.1. Petroleum :

Among the existing refineries only İpraş and İzmir (Aliağa) have small desulfurization units. Production of sulfur in 1973 is :

İpraş	6,128 tons
İzmir	567 tons

These two refineries' sulfur production is estimated to reach the level of 9,000 tons each in 1977 and 12,000 tons in 1980 in parallel to the completion of cracking unit. (151)

4.2.4.2. Natural Gas :

Turkey has actualy no considerable natural gas production. There is a project of bringing natural gas from Iraq, in which case 80,000 tons per year sulfur production during 1976-1980, and 100,000 tons per year during 1981-1995 is considered.

The production cost of sulfur, if the project is realized, is shown in Table 40. (150)

TABLE 37 : PRODUCTION AND DEMAND FOR GYPSUM IN TURKEY (111) (Production = Demand)

Years	1000 tons
1960	80
1961	100
1962	140
1963	180
1964	200
1965	220
1966	250
1967	275
1968	380
1969	417
1970	550
1971	605
1972	650
1973	720
1977	1,000
1982	1,400

TABLE 38 : GYPSUM RESERVES IN TURKEY (55)

Locations	Estimated reserves (million tons)	Approximate SO_3 content (%)	Total S content (million tons)
Sivas	1,000	46	184
Çankırı	100	35	14
Niğde	140	46.5	25
Beypazarı-Eskişehir	100	n.a	
Siirt	15	n.a	
Kayseri	4.5	n.a	
TOTAL	1,359.5		230 (roughly)

TABLE 39 : TURKISH REFINERIES AS POTENTIAL SULFUR SUPPLIERS (156)

Refineries	Crude oil capacity (million tons/yr)	Average sulfur content, %	Recoverable Sulfur (at 30 % yield) tons/yr	Actual Recovery
-Mersin (Ataş)	4.4	2.4	32,400	
-Batman	1.2	4.5	16,200	
İzmit (İpraş)	5.5			6,000
	-2.5	2.4	18,000	
	-3.0	4.5	40,400	
İzmir (Aliağa)	3.0			600
	-1.0	2.4	7,200	
	-2.0	4.5	27,000	
Total (at full capacity)	14.1		141,200	6,600
Total (at 2/3 capacity)			94,100	

TABLE 40 : SULFUR COST (US $/ton) in IRAQ PROJECT (150)

	With full recovery			With partial recovery		
	1976-80	1981-87	1988 and after	1976-80	1981-87	1988 and after
H_2S removal (x)	7.01	9.27	3.95	8.92	10.83	3.95
S recovery	10.14	9.11	2.96	13.50	11.79	2.96
Total (xx)	17.15	18.38	6.91	22.42	22.62	6.91

(x) : to be included in the cost of S in the case that natural gas is used for energy.

(xx) : cost of S in the case that natural gas is used for ammonia production.

TABLE 41 : PRODUCTION, IMPORTS AND DEMAND FOR SULFUR İN TURKEY (tons)

	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	1973	1977 (x)	1982 (x)
Production (pure S)	18.540	19.430	22,200	22,300	22.650	25.030	24.180	25.700	26.760	23,020	22.455	17.750	87.000	137.000
Imports (total)	26	249	210	103	105	602	10.132	14.602	112	3,179	751	82	6,000	-
(Prod.+ Imports)	18.600	19.700	22,400	22.400	25.800	25.600	37.000	40.300	26.900	26.200	22.500	17.800	93.000	137.000
Demand	12,000	16.000	20.000	24,500	28.500	32,600	37.000	41.000	45.000	49.000	53.000	57.000	93.000	137.000
Surplus(+) or Deficit (-)	6.600	3.700	2.400	-2,100	-2.700	-7.000	-	- 700	-18.100	-16.800	-30.500	-39.200		

(x) : 3rd Five Year Development Plan targets.

TABLE 42 : SULFUR DEMAND OF EXISTING AND PROJECTED SULFURIC ACID PLANTS (1000 tons)

Plants	Nominal acid (100%) capacity, tons/yr	1974	1975	1976	1977	1978	1979	1980	1981	1982
Karabük	19.0	8.0	5.9	5.9	5.9	5.9	5.9	5.9	5.9	5.9
MKEK	13.7	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2
Koruma	9.0	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8
BenzoKimya	3.8	1.2	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Arılar	5.8	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9
Sub-total	51.3	18.1	16.8	16.8	16.8	16.8	16.8	16.8	16.8	16.8
Ege Gübre San (x)	172.3	-	-	-	36.6	44.9	53.0	56.2	56.2	56.2
Tekfen (x)	141.6	-	-	-	-	-	-	-	37.8	46.2
Tegesan (x)	132.2	-	27.6	34.5	41.0	43.1	43.1	43.1	43.1	43.1
İşkur (x)	309.0	-	-	68.9	84.8	100.8	100.8	100.8	100.8	100.8
Sub-total	755.1		27.6	103.4	162.4	188.8	196.9	200.1	237.9	246.3
Demand										
Grand-total	806.4	18.1	44.4	120.2	179.2	205.6	213.7	215.9	254.7	263.1
Production		35.0	35.0	35.0	87.0(xx)	87.0	87.0	87.0	87.0	137.0(xx)
Deficit		-16.9	9.4	85.2	92.2	118.6	126.7	129.9	157.7	126.1

Note: (x) Last four new plants suppose to import sulfur.

(xx) 3rd Five Year Development Plant Targets.

TABLE 43 : TURKISH PYRITES PRODUCTIONS PROJECTION (1000 tons)

	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986
Etibank Ergani (%42 S)														
floatation pyrites	120	225	225	225	225	225	225	225	225	225	225	225	225	-
Etibank Murgul (%46 S)														
floatation pyrites	20	30	35	35	35	35	35	35	35	35	35	-	-	-
Etibank Küre (%45.5 S)														
cupric pyrites	100	125	125	125	125	125	125	125	-	-	-	-	-	-
KBI Murgul (%46 S) floatation pyrites	40	120	230	230	230	230	230	230	180	180	180	180	180	180
KBI Küre (%43.5 S)														
cupric pyrites	180	180	180	180	180	180	180	180	180	180	-	-	-	-
Etibank KeçiborluS residues														
a. 60 % S	20	20	20	20	20	20	20	20	20	20	-	-	-	-
b. 20 % S	30	30	30	30	30	30	30	30	30	30	-	-	-	-
Total (45% S) average)	510	730	845	845	845	845	845	845	670	670	440	405	405	180
S-equivalent	229	328	380	380	380	380	380	380	302	302	198	182	182	81
TOTAL Demand (Table 44) (S-eq)		193.1	229.4	326.8	358.5	368.5	368.5	368.5	368.5	368.5	368.5	368.5	368.5	368.5
Deficit (+) (S-eq.)		-134.9	-150.6	-53.2	**-21.5**	-11.5	-11.5	-11.5	66.5	66.5	170.5	186.5	186.5	287.5

TABLE 44 : PYRITES DEMAND OF EXISTING SULFURIC ACID PLANTS IN TURKEY (1000 tons)

Plants	Nominal acid (100 %) capacity tons/year	1974	1975	1976	1977	1978	1982
Samsun (Azot)	206.0	113.2	140.2	140.2	140.2	140.2	140.2
Bandırma	93.9	63.9	63.9	63.9	63.9	63.9	63.9
Mersin	210.2	114.5	135.8	143.2	143.2	143.2	143.2
İskenderun	225.0	51.1	99.5	122.5	145.7	153.0	153.0
Samsun (KBI)	339.5	51.1	150.1	184.8	219.5	231.0	231.0
Ergani	115.5	25.9	51.1	62.6	74.9	78.6	78.6
Murgul	31.4	9.5	9.5	9.5	9.5	9.5	9.5
Total pyrites demand		429.2	650.1	726.7	796.9	819.4	819.4
Total S-equivalent		193.1	292.4	326.8	358.5	368.5	368.5

conversion factor : 1 ton of 100 % H_2SO_4 consumes 0.681 ton of 45 % S containing pyrites.

TABLE 45 : SUMMARY OF SULFUR RESOURCES OF TURKEY (1000 tons)

	Estimated Reserves	Sulfur Content	Possible or supposed production
1. Native Sulfur		573.5	8.1 % of total 35.0 tons S/yr.
	303.5 (43.3 % S)	131.2	
	996.9 (39.5 % S)	393.5	
	122.9 (60.0 % S)	73.8	
	230.0 (32.6 % S)	75.0	
2. Pyrites			
- pyrite concentrates			38.6 % of total 167.4 "
Ergani	225.0 per yr (42 % S)		94.5 "
Murgul	35.0 per yr (46 % S)		16.1 "
Küre	1.309.9 (45.4 % S)	595.0	55.8 "
- Copper concentrates			51.8 % of total 224.6 "
Murgul	220.0 per yr. (46 % S)		101.2 "
Küre	130.0 per yr (45.5 %)		78.4 "
Espiye	2.300.0 (39.5 % S)	909.0	45.0 "
3. Gypsum	1.359.5	230.0	n.a
4. Petroleum			1.5% of total 6.6 "
Total			433.6

TABLE 46 : TOTAL DEFICIT OF RAW MATERIALS (in terms of 1000 tons of S)

Deficit	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986
From Pyrites	-134.9	-150.6	-53.2	-21.5	-11.5	-11.5	-11.5	66.5	66.5	170.5	186.5	186.5	287.5
From Elemental S	- 16.9	9.4	35.2	92.2	118.6	126.7	129.9	267.7	126.1	126.1	126.1	126.1	126.1
Total Deficit(+)	-151.8	-141.2	32.0	70.7	107.1	115.2	118.4	334.2	192.6	296.6	312.6	312.6	413.6
Total Deficit	-151.8	-168.8	-71.4	-91.7	-81.7	-81.7	-81.7	-15.7	-55.7	50.3	66.3	66.3	167.3

(Exluding the S requirements of of 4 new s.a. projects)

4.2.5. CONCLUSION :

a. Domestic resources of elemental sulfur (brimstone) constitutes 8.1 % of total sulfur supply nowadays; it is not a reliable source for the new projects unless some-other new occurences are certified.

b. The major sulfur supplier is the pyrites at present; considering the present level of consumption at the existing plants, these deposits can stand until 1986. The mining research activities on pyrites has to be mobilized for further needs.

c. Copper smelter gases as a source for sulfur, are bound to metallurgically aimed plants.

d. Known gypsum reserves (natural gypsum and anhydrite) offer the possibility of using them as a raw material for sulfuric acid industry.

e. Sulfur from petroleum provides a very small potential.

CHAPTER 5

PRODUCTION METHODS

Before 1900 all the sulfuric acid plants were operating with the chamber process. The contact process had become very important in Europe because of the need for oleums and high strength acid for sulfonation, particularly in the dye industry. A substantial number of contact plants were built in the period 1900-1925, using platinum catalyst. The wet contact process was introduced which exploits the fact that the vanadium pentoxide catalyst is not contaminated by sulfurdioxide gases containing water vapor. The wet contact process offers the possibility of producing sulfuric acid directly from the hydrogen sulfide obtained in coke-oven plants and refineries or contained in natural gas, unless preference is given to the production of elementary sulfur.

In the middle 1920 s, vanadium catalyst came into use and has gradually completely replaced platinum. About 1930, American practice demonstrated that the contact process could compete with the chamber process regardless of strength of acid desired.

There are three main reasons for the considerable growth of the contact sulfuric acid process and the corresponding decline of the former lead chamber and tower process :

- the increasing demand for concentrated sulfuric acid, the principal consumer being the organic chemical industry,
- the increasing demand for high-purity acid;
- the reduction in contact acid production costs as a result of design improvements.

The most modern contribution to the contact technique is the double catalysis process, developed by Farben-Fabriken Bayer AG in 1960. By this process the equilibrium of the reaction is shifted to the sulfur trioxide side through intermediate absorption of the sulfur trioxide. The higher conversion, upto 99.5 % and more, permits an increase of the sulfuric acid yield and decrease of air pollution to an appreciable extend. Some of the existing plants are modified to adopt them to the application of this process.

Table 47 lists the sulfuric acid plants recently built or on-erection in the World, totally 61 projects which have the following distribution of production methods: 1 Polish process (unspecified), 5 replacement and expansions projects, 1 Wellman-Lord process, 1 regeneration unit, 1 Nisson Chemical Industries Technology, 1 Raska-Petersen process, 1 Kowa Selko's process, 47 double catalysis process of which 7 Ugine Kuhlman's, 20 Bayer's, 2 Lurgi's, 17 Monsanto/Sim-Chem's, 1 Chemico's and 2 Chemibau's.

The sulfur dioxide required for the sulfuric acid is produced by roasting pyrites and other sulfidic ores in turbulent layer furnaces, multiple hearth furnaces and rotary kilns, or by combustion of sulfur and hydrogen sulfide.

Other raw materials are sulfates such as gypsum or anhydrite, the products in that case being sulfuric acid and cement.

When large amounts of less concentrated sulfuric acid are required, e.g. in the fertilizer industry where 78 % sulfuric acid is used for the production of normal superphophate, it is often more economical to dilute the highly concentrated contact acid at the place where it is needed, thus saving transport costs.

5.1. Chamber Process

5.1.1. Production Method

A typical flowchart for the chamber process is presented in Fig. 3. The process starts when either the sulfur or pyrite is burned and the hot gases are conducted through a combustion chamber, which also may collected some dust. The hot gaseous mixture passes up through the Glover tower, where it is met by the downward flow of the nitrous vitriol produced in the Gay-Lussac tower and of the dilute acid from the chambers. Nitrous vitriol is a solution of nitrosylsulfuric acid ($ONOSO_2OH$) in sulfuric acid, and is also called nitrose.

From the Glover tower the entire output of the plant may be obtained as 60°Bé (77.67 %) sulfuric acid. The nitrogen oxides from an ammonia oxidation unit are also introduced into the gas stream, after the gas has been cooled by its passage up the Glover tower. The cooled gases flow to the chambers, where water is sprayed into them and 50 to 55°Bé acid condenses. This acid is pumped to the Glover tower for concentration to 60°Bé.Finally, unreacted gases pass to the Gay-Lussac tower for the absorption of the nitrogen oxides in some of the 60°Bé Glover acid, thus producing the Gay-Lussac, or the nitrous vitriol, acid.

The conversion of the sulfur dioxide to sulfuric acid involves many fairly complex chemical changes. The overall reaction is :

$$SO_2(g) + \frac{1}{2} O_2(g) + H_2O(l) \longrightarrow H_2SO_4\ (l)$$

$$\Delta H_{25} = -54.6\text{kcal}$$

Reaction steps are :

$2NO + O_2 \longrightarrow 2NO_2$ at all parts of the system

$SO_2 + H_2O \longrightarrow H_2SO_3$ in Glover tower, chambers

$NO + NO_2 + 2H_2SO_4 \longrightarrow$ Gay-Lussac tower, chambers

$2ONOSO_2OH + H_2O$ (partly)

$H_2SO_3 + 2HNO_2 \longrightarrow$ Glover tower, chambers

$H_2SO_4 + 2NO + H_2O$

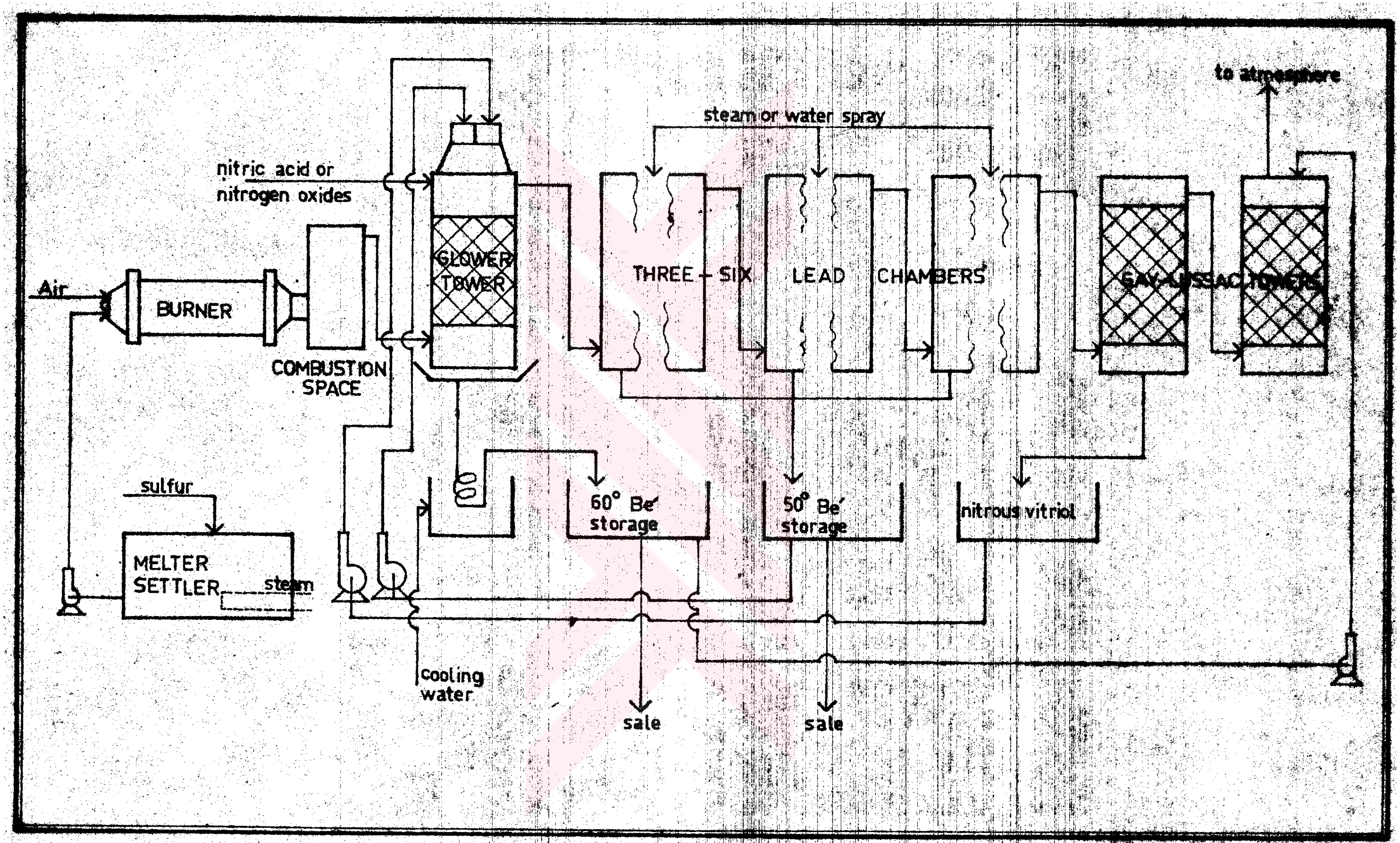

FIGURE 3: FLOWSHEET OF PRODUCTION BY THE CHAMBER PROCESS (132)

The important characteristics of the chamber process are the circulation of the catalytic oxides of nitrogen and their recovery at the end of the process. The heat of reaction must be dissipated through the chamber walls to secure the desired favorable equilibriums.

5.1.2. Effluent Control in Chamber Plants :

Emissions from chamber plants are quite different from the contact process plants. Most chamber plants are of small capacity, ranging from 40 to a little over 100 short tons per day of 100 % sulfuric acid equivalent. The chamber process produces acid of about 78 % which **finds** little use outside the acidulation of phosphate rock to produce simple superphosphate fertilizers. Tail gas emissions from chamber plants are approximately as follows :

Flowrate	100 to 160 scf/ton of acid (100% acid)
SO_2 content	1500 to 4000 ppm
Acid mist control	5 to 50 mg/scf
NO_2 content	1000 ppm
NO content	500 ppm

Emissions from chamber plants can be as much of a problem as those from contact plants. Because the chamber process is gradually disappearing, little effort has been expended on control of this dual emission problem of sulfurdioxide and nitrogen oxides.

Processes applicable to contact plants are not suitable for removal of nitrogen oxides and likewise, processes applicable to nitric acid plants for NO_x control are not best for sulfurdioxide control. Mist loadings are similar to those for nonoleum contact plants, and the same types of mist control devices are applicable.

Various processes have been reviewed for control of this dual problem, none of which may be considered feasible. A cursory review of the control cost for the sodium hydroxide absorption process when applied to a rather large capacity chamber plant gave a control cost of over 8 $ per short ton, far in excess of the cost for contact plant control processes. Based upon this finding, it is considered very doubtful that a chamber acid plant, if faced with a choice of installing a control system or shutting down, could justify economically the installation of a control system.

5.2.1. Classical Contact Process

The contact and the chamber processes use the same raw materials, i.e., sulfur principally and some sulfide ores. Generally, about 9 % sulfurdioxide is furnished to the plant when sulfur is burned, though this percentage can be increased. If the raw material is dust containing gases such as roaster gases, metallurgical plant exit gases and the like, the gases are cleaned in cyclones and/or hot electro-precipitators, then in scrubbers and wet electro-precipitators; moreover, the gases are cooled and subsequently dried by means of concentrated sulfuric acid.

The sulfurdioxide burner gas for the contact process may contain, in addition to dust, carbon dioxide, nitrogen, and oxygen, such impurities as chlorine, arsenic and fluorine. The last two impurities are present only when materials other than elemental sulfur are burned. To prevent corrosion from the burner gases, it is customary to dry the air for burning the sulfur and oxidizing the sulfur dioxide in the converter and to dry the roaster gases before oxidizing the sulfur dioxide. Such drying is done in towers, usually with 93 to 98 % sulfuric acid. The sulfur burner gas has much of its heat removed in waste-heat boilers for the generation of steam. If a sulfide ore is roasted, efficient dust collectors, cooling and scrubbing towers and electrical acid mist precipitators may be added.

Before the gases can be taken to the first stage of the converter, they are adjusted to the minimum temperature at which the catalyst will rapidly increase the speed of the reaction, usually 410 to 440 °C. The gases must be cooled between catalyst stages to achieve high conversion. For this purpose, cold air may be introduced or boilers, steam efficiency superheaters, or tubular heat exchanger may be employed. Heat exchangers usually consist of large vertical cylinders containing many small tubes. The sulfur trioxide gas usually passes through the tubes, and the sulfur dioxide gas surrounds the tubes.

The chemical conversion of sulfur dioxide to sulfur trioxide is designed to maximize this conversion by taking into consideration that :

1. Equilibrium is an inverse function of temperature and a direct function of oxygen ratio to sulfur-dioxide.

2. Rate of reaction is a direct function of temperature.

3. Composition and ratio of amount of catalyst to amount of sulfurtrioxide formed affect the rate of conversion or the kinetics of the reaction.

The commercialization of these basic conditions makes possible high overall conversion up to 98 % or more by using a multipass converter wherein, at an entering temperature of 410 to 430 °C, the major part of the conversion (about 75 %) is obtained, with an exit temperature from the first catalyst bed of upto 600 °C or more, the latter temperature depending largely on concentration of sulfurdioxide in the gas. The successive lowering of the temperature between stages ensures an overall higher conversion.

Although the converter is the heart of a contact sulfuric acid plant, there are many variables. All these should be optimized to secure maximum industrial results.

A concentration of acid between 98.5 and 99 % sulfuric acid is the most efficient agent for absorption. Hence acid of this strength is used for the final absorber before the waste gas is vented to the atmosphere. Since the absorbing acid is continuously becoming more concentrated, it is necessary to provide some means for diluting that part of the acid discharged from the final absorber which is to be recirculated. Also, the absorbing acid must be cooled. Diluting the recirculating acid is done by adding spent or dilute sulfuric acid or water in the amount required, withdrawing from the system any excess acid for sale.

The 20 % oleum is made in the oleum absorber by passing cooled 98.3 to 98.5 % acid over this tower. If an oleum of 60 to 65 % is wanted, it may be prepared by distilling the 30 or 35 % oleum in steel boilers. The trioxide driven off is usually condensed and then added to 20 % or stronger oleum to get the desired 60 to 65 % concentration.

Information related to the simulation program for the design to reflect shifting uncontrollable variables is deeply illustrated by A.C. Homme and D.F. Othmer in Industrial and Engineering Chemistry, vol. 53, No.12, Dec. 1961.

5.2.2. Wet Contact Process (Figure 4)

Gases containing at least 10 % hydrogen sulfide from coking plants and mineral oil refineries from solid fuel gasification or low-temperature carbonization processes, from the purification of natural gas from the production of carbon disulfide and from the textile fibre industry are the main raw materials. Gases containing less than 10 % hydrogen sulfide must be burned with additional fuel (e.g. fuel gas, fuel oil or sulfur). Sulfuric acid having a concentration of 60°Bé (78 % acid) is produced.

The wet contact process is distinguished from the natural contact process by the fact that the latter treats dry sulfurdioxide-air mixtures while the former uses moist gas. The hydrogen sulfide in the initial gas is first burned to sulfurdioxide and water. The sulfurdioxide is converted to sulfur trioxide which forms sulfuric acid with the water vapor from the reaction.

The gases containing sulfurdioxide and water vapor enter the converter at approximately 440°C. As in the classical process, the sulfurdioxide is catalytically

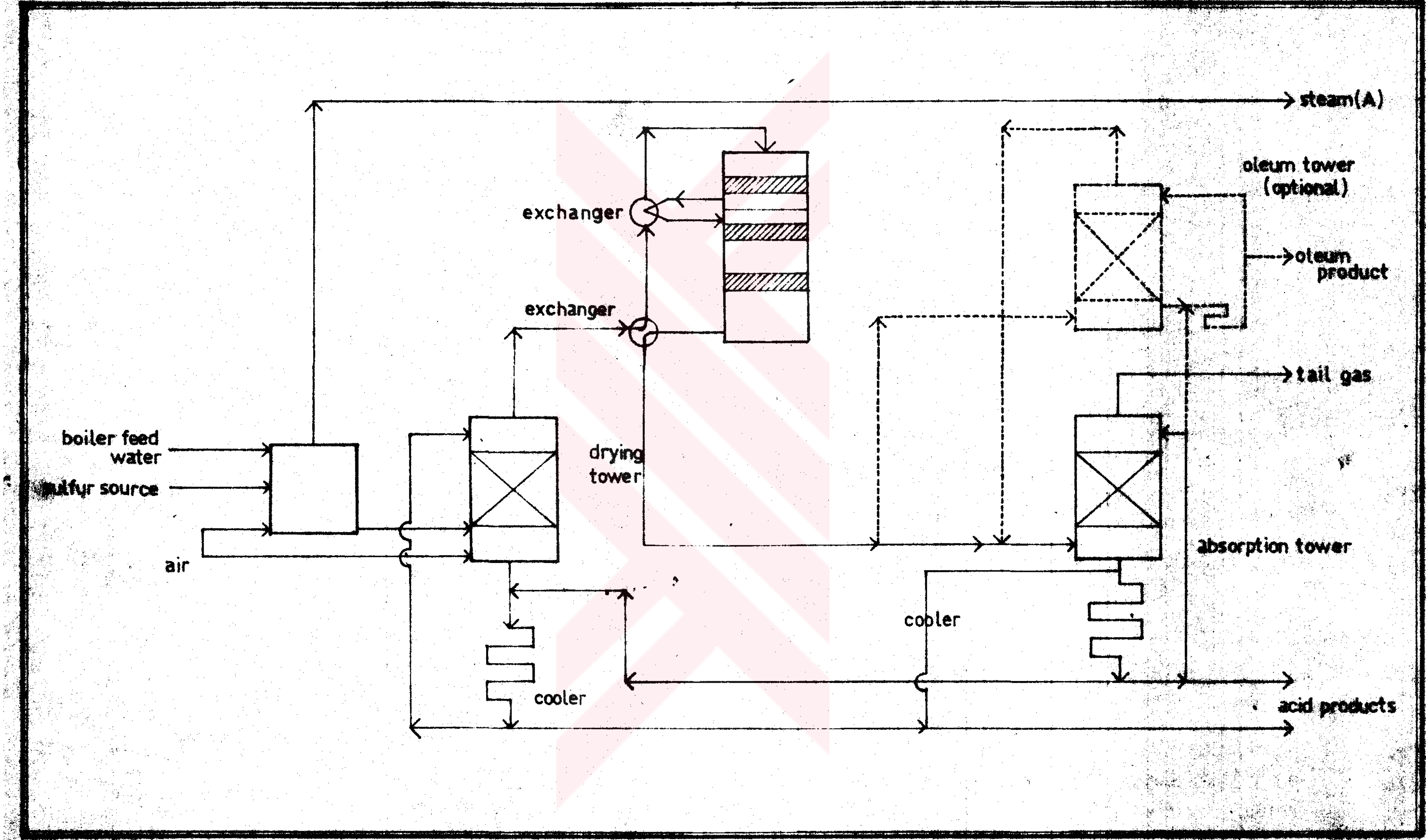

FIGURE 4: FLOW DIAGRAM OF WET GAS CONTACT PLANT WITH THREE CONVERSION STAGES (133)
(type 1.3)

oxidized to sulfur trioxide. In order to ensure optimum conversion, the reaction temperature ahead of each tray is maintained at a predetermined degree by addition of cold air. The gas containing water vapor and sulfur trioxide, which leaves the converter, is irrigated with circulating sulfuric acid in a condensation tower. The condensation heat and the sensible heat are removed from the circulating acid by irrigation coolers. Part of the circulating acid is continuously removed from the process as product. The sulfuric acid mist not removed during the acid washing is precipitated in ceramic pressure filters.

5.2.3. Double Catalysis Process (Figure 5)

The double catalysis process was developed from the classical contact process to attain two objectives: an increase of plant production and a reduction of the sulfurdioxide content of the exit gas to meet the increasing demands regarding the prevention of air pollution. At the same time, this process offers the possibility of treating gases containing 9-10 % sulfurdioxide by volume without air pollution. On the whole the double catalysis ensures higher sulfur trioxide yields without increasing the production costs.Gases with sulfurdioxide contents down to 6 % can be converted autothermally, i.e. without extraneous fuel. Therefore, the double catalysis permits to treat also effluent

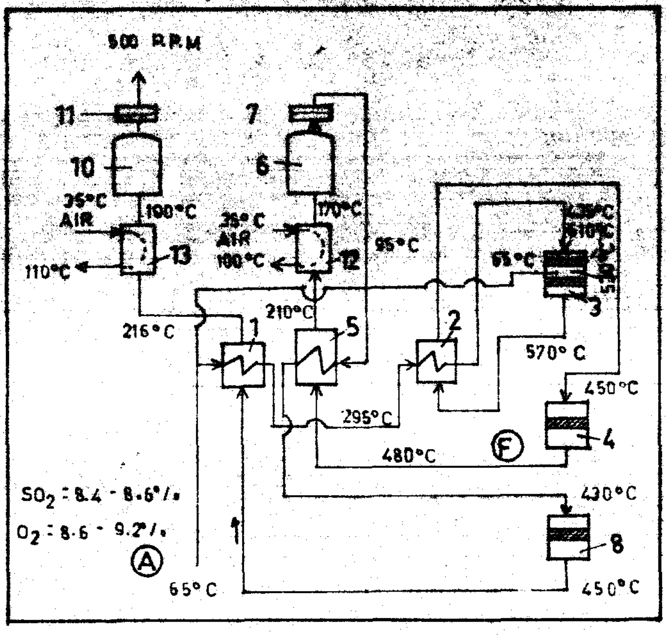

FIGURE 5: FLOWSHEET OF AN OLDER DOUBLE CONTACT PROCESS (47)

1. HEAT EXCHANGER
2. HEAT EXCHANGER
3. FIRST CATALYST CHAMBER
4. SECOND CATALYST CHAMBER
5. HEAT EXCHANGER
6. SO_3 ABSORPTION TOWER
7. MIST COLLECTOR
8. THIRD CATALYST CHAMBER
10. FINAL ABSORPTION TOWER
11. MIST COLLECTOR
12. SO_3 COOLER
13. SO_3 COOLER

gases of metallurgical plants, e.g. from combined roasting and sintering processes.

The reaction equilibrium of the contact processes

$$2SO_2 + O_2 \longrightarrow 2SO_3$$

is shifted, in the case of the double catalysis, to the sulfurtrioxide by removing from the reaction mixture, through intermediate absorption, the sulfur trioxide already formed.

The sulfurdioxide/sulfur trioxide gas, preconverted in the first trays of a multi-stage converter, passes into a heat exchanger where it is cooled, and then into an intermediate absorber where it is irrigated with concentrated sulfuric acid which absorbs the sulfur trioxide. The sulfur trioxide -free reaction gas is reheated to approximately 400 °C by heat exchange with the hot contact gases and then conveyed to the last stage of the converter where the remaining sulfurdioxide is converted to sulfur trioxide.

5.2.4 Double Contact/Double Absorption Process

Figure 6 shows the new patented DC/DA process, this process achieves a double contact reaction ahd absorption somewhat similar to the older process except that higher conversion efficiencies can be initially and finally obtained at a greatly reduced investment cost, because of substantial reduction in heat exchanger surface, while operating under approximately the same conditions. The new process also permits more flexible operation, more stable catalyst bed temperatures and great savings in start-up time. When the inlet and exit temperatures were the same in the older process, heat exchange surface was infinite, which is not the case with the DC/DA process. Since gas entering the final catalyst bed is not entirely dependent upon the exit gas temperature leaving chamber 4, there is very little chance of upset operating conditions in the final catalyst bed.

In the DC/DA process conversion efficiencies in excess of 99.9 % may be achieved. Gas effluents lower than 100 ppm sulfurdioxide can also be achieved with modifications of some equipment shown in Fig.6.

One of the main advantages of the new process is that existing plants can easily be modified by addition of heat exchangers, an absorption tower, pump,tank, coolers, etc. Addition of new equipment in many cases will increase plant production capacities by approximately 25 to 30 %.

The DC/DA plant has another advantage over other processes in that gas returned to the converter after initial absorption is preheated in heat exchangers at extremely high temperature levels, thereby reducing heat exchanger size and cost.

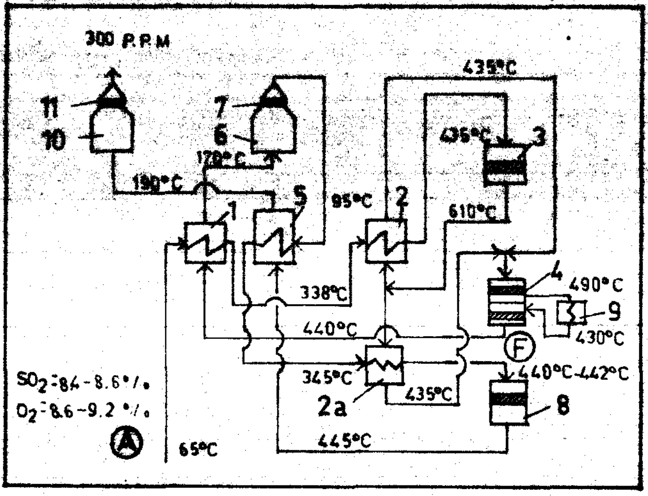

FIGURE 6: .FLOWSEET OF DOUBLE CATALYSIS/DOUBLE ABSORPTION PROCESS (47)

1. HEAT EXCHANGER
2. HEAT EXCHANGER
2a. HEAT EXCHANGER
3. FIRST CATALYST CHAMBER
4. SECOND CATALYST CHAMBER
5. HEAT EXCHANGER
6. SO_3 ABSORPTION TOWER
7. MIST SEPARATOR
8. THIRD CATALYST CHAMBER
10. FINAL ABSORPTION TOWER
11. MIST SEPARATOR

Existing plants operating on sulfurdioxide gas strengths of 8 to 8.5 % can be easily converted to the new DC/DA process with a small capital investment, and then operated on 10.5 to 11 % sulfurdioxide.

Besides the economic incentive of sulfur cost savings, there are other reasons for acid producers to seek higher conversion efficiency :

1. Attainment of more conversion efficiency for existing plants usually requires the installation of additional catalyst and one or more reactor (converter) stages. The additional earnings from the sale or use of the extra acid can permit high returns on the extra investment. Payouts range from 3 to 10 months in some cases. (Fig. 7.)

2. More efficient use of the available sulfur raw material to produce the maximum amount of acid from a limited supply.

3. Reduction of the amount and concentration of sulfurdioxide emitted to atmosphere from the plant exit stack.

4. Potential reduction in the investment cost for new plants by the trial of new technology in existing plants.

5.2.5. Chamber Process vs. Contact Process

A.M. Fairlie's generalizations :

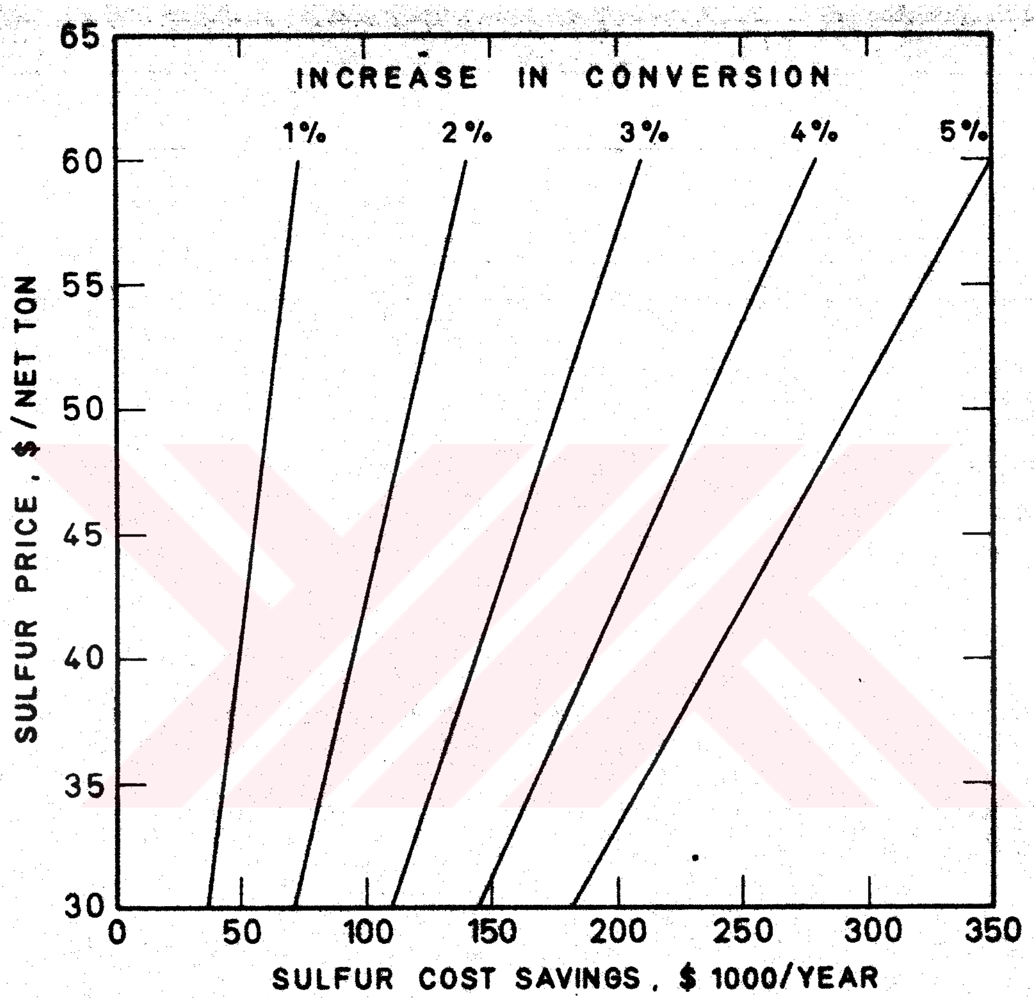

FIGURE 7: Potential sulfur savings (47) in DC/DA Process.

1. If 98 % acid or oleum is required, a contact plant must be used.

2. Oil of vitriol (66°Bé, 93.2 %) can almost always be made more cheaply by diluting contact acid than by concentrating chamber acid.

3. The air-cooled lead chamber is obsolescent, as are the Mannheim and the Tentelew platinum contact process.

4. For 60°Bé (77.67 %) and weaker acids, the choice between liquid cooled chambers, a vanadium contact plant, and a platinum contact plant is open, local conditions will decide each proposed installations. Much of the published data, of course, is written by persons financially interested in one certain angle of the matter.

5. The cost of catalyst, and hence the interest charges, varies greatly from time to time.

6. The chamber plant has greater flexibility in production rate than the contact plants.

7. The contact plant has greater flexibility in the strength of acid produced.

8. High-pressure chamber plants, e.g. 30 to 50 atmospheres, as suggested by E. Berl, are a future possibility, through offering great difficulties of design.

5.2.6. Effluent Control in Integrated Contact Process Plants (129)

Four basic types of integrated contact process plants have been designated for existing plants:

1.1. for sulfur burning contact plants with 3 conversion stages
1.2. for sulfur burning contact plants with 4 conversion stages
1.3. for wet gas contact plants with 3 conversion stages
1.4. for wet gas contact plants with 4 conversion stages.

Plant Classification 1.1 :

These plants, for the most part built prior to 1960 in the United States, may produce various grades of acid from 93 % sulfuric acid to oleum, or combination thereof.

Typical operating characteristics of these plants are as follows where operating at design conditions:

SO_2 in converter feed 7.5 to 8.5 mol %
Conversion of SO_2 to SO_3 95 to 96 %

Characteristics of the tail gas emissions from these plants at design conditions are as follows:

Maximum flow	91,800 SCF/ton acid (as 100% acid)
SO_2 content	3,000 to 5,000 ppm
Acid mist	2 to 20 mg/SCF
SO_3 content	0.3 to 1.3 ppm
Oxygen	9 to 11 % by volume
Water	nil
Inert gas (N_2, A, CO_2, etc)	remainder
Temperature	150° to 180°F

Sulfur losses per ton of acid produced (as 100 % acid) are as follows at design conditions :

	tons of sulfur
As SO_2	0.014 to 0.017
As mist when producing 99%acid	0.002 maximum
As mist when producing oleums	0.005 maximum

These plants were in many cases capable of producing acid at rates significantly higher than design but at a lower efficiency and with consequently by greater sulfur losses. This is due to design factors included in the plant designs which would permit operation at higher capacities. Often plants were designed to produce as much as 50 % excess capacity at a lower conversion efficiency, and with excess pressure capability in the blower and additional catalyst space in the converter to permit reaching either design capacity with dirty catalyst or higher capacity by addition of catalyst.

This type of plant can take maximum advantage of either a tail gas recovery process, which return recovered sulfurdioxide to the plant, or an add-on dual absorption process, by operating at maximum production rate and still keeping emissions within reasonable limitations after inclusion of a control system. Many older plants in U.S.A. are congested and surrounded by other facilities which may make addition of a new equipment for emission control very difficult.

Sulfur burning plants always have sufficient heat to produce steam in excess of plant requirements for heating and mechanical drives. The use of steam generated is usually dictated by adjacent facilities. If the acid plant is associated with a wet process phosphoric acid plant, much of the steam can be utilized on the concentration of phosphoric acid. If the acid plant is associated with a refinery or other process plant, excess steam can usually be used in the appropriate steam header. In the case where excess steam has no user available, driving a turbo generator can reduce plant power requirements.

The production of oleum effects only the acid mist emission from the plant, mist from oleum plants being more finely divided than that from plants producing acid grades at less than 99 %, and requiring a different type of mist control device for such a plant for effective control. Tail gas treatment systems which control both mist and sulfurdioxide would be less affected by the grades of products produced.

Operating plants falling within this classification vary in capacity from 50 tons per day to 4,000 tons per day; however no single unit in these plants exceeds about 750 tons per day.

Plant Classification 1.2

This type plant is a typical modern 4-stage conversion sulfur burning acid plant. These plants may produce a variety of acid grades ranging from 93 % sulfuric acid to various oleum grades, or combination thereof.

Typical operating characteristics of these plants are as follows when operating at design conditions: SO_2 in converter feed, 7.5 to 8.5 mol %; conversion of SO_2 to SO_3, 96 to 98 %.

Characteristics of the tail gas emission from these plants at design conditions are as follows:

Maximum rate	90,800 SCF/ton acid (as 100%acid)
SO_2 content	1,500 to 4,000 ppm
Acid mist	2 to 20 mg/SCF
SO_3 content	0.3 to 1.3 ppm
Oxygen	9 to 11 % by volume
Water	nil
Inert gas (N_2, A, CO_2, etc)	Remainder
Temperature	150° to 180°F

Sulfur losses per ton of acid produced (as 100 % acid) are as follows at design conditions :

	tons of sulfur
As SO_2	0.007 to 0.014
As mist when producing 99% acid	0.002 maximum
As mist when producing oleum	0.005 maximum

The majority of these plants are probably being operated at or near their design capacities today, and the newest and largest at 98 % conversion. Comments with respect to steam production and optional oleum producing facilities included with the description of class 1.1 apply equally to class 1.2.

Operating plants in classification 1.2 generally have a capacity of 250 tons per day or more. The largest plants do not exceed 2,000 tons per day in a single train, though some plants have multiple units.

It is beyond this point where structural problems apparently outweigh the cost advantage of a single train plant, using the conventional acid.

A number of plants are designed for additional capacity at reduced efficiency with provisions for additional catalyst. These plants could improve conversion rate and reduce sulfur emission by addition of catalyst while continuing to operate at the basic design rate, although the conversion improvement is limited. These plants are technically suited to add-on dual absorption or tail gas recovery systems of most types. Most were originally built with some form of mist control device to reduce the acid mist in the tail gas, and the 2 mg/SCF mist level in the tail gas reflects plants so equipped.

The class 1.2 plants are not likely to be as cramped for space required for an emission control system as other class 1.1 plants, although this remains a distinct problem. Finding space for an additional 28' diameter absorber and 35' diameter converter with attendant duck work and heat exchangers, such as would be required for a large plant, will not be simple.Tail gas recovery processes are more attractive for larger plants such as are encounteredin class 1.2.

Plant Classification 1.3

These plants may produce various grades of acid from 93 % H_2SO_4 to oleum using a variety of sulfur sources, singularly or in combination.Sulfur sources include sulfurdioxide resulting from roasting of various copper, zinc and other ore concentrates, burning of spent alkylation acid or hydrogen sulfide from refinery operations, roasting of iron pyrites, recovery of sulfurdioxide from copper converter and reverberatory furnace flues, and a few others.

While these plants differ widely from each other in detail, they all lend themselves to similar methods of emission control. All generally require similar types of in-plant control systems, but different from these suitable for sulfur burning plants, as well as generally larger add-on systems for a given plant capacity because of the normally larger quantities of gas to be handled and sulfur values to be recovered. Typical operating characteristics of these plants when operating at design conditions are given below for various feedstock:

Feedstock	SO_2 in converter feed, mol %	Conversion SO_2 to SO_3,%
H_2S	7	94 to 96
Pyrites	6.5 to 7.5	94 to 96
Acid sludge	6 to 8	94 to 96
Copper converter gas	3 to 7	90 to 95
Roaster gas	5 to 7	94 to 96

Characteristics of the tail gas emissions from these plants may be expected to fall in the following ranges:

Feedstock	Maximum rate SCF/ton of acid (as 100% acid)	SO_2 content ppm	Acid mist, mg/SCF Producing 99% acid	Acid mist, mg/SCF Producing oleum
H_2S	100,000	3,000 to 5,000	2 to 20	5 to 50
Pyrites	109,000	2,500 to 5,000	2 to 20	5 to 50
Acidsludge	119,000	2,500 to 4,000	2 to 20	5 to 50
Copper converter gas	192,000	2,000 to 10,000	2 to 20	5 to 50
Roaster gas	145,000	2,000 to 5,000	2 to 20	5 to 50

With this type of plant the variation in the other components in the tail gas varies so widely that any compositions given would be meaningless. Sulfur losses per ton of acid produced (as 100 % acid) are as follows at design conditions:

	Sulfur Loss, tons		
	As SO_2	As acid mist	
Feedstock		Producing 99 % acid	Producing oleum
H_2S	0.014 to 0.021	0.002 max	0.006 max
Pyrites	0.014 to 0.021	0.002 max	0.006 max
Acid sludge	0.014 to 0.021	0.003 max	0.007 max
Copper converter gas	0.017 to 0.036	0.004 max	0.011 max
Roaster gas	0.014 to 0.021	0.003 max	0.008 max

Plants based on pyrites, hydrogensulfide or acid sludge (spent acid) will have excess heat available for steam production and in most cases will, in fact, include waste heat boilers. Plants based on roaster or smelter gases from metallurgical processes are not normally steam producers.

Many plants of this type operate on combinations of feedstocks and include sulfur as well as one or more of the feedstocks mentioned before. These plants require that the gas be cooled and cleaned before introduction into the converter system. Except in the case of plants based on copper converter gas, most methods of emission control can be applied. The cyclical nature of copper converter operation makes the application of the dual absorption process, or even careful converter control much more difficult.

Many plants of this type are located in congested metallurgical complexes and systems with minimum space requirements may be referred. Those locations with several units close together recovering acid from smelters may favorably utilize several tail gas scrubbing unit feeding to a single recovery system.

Operating Plants of this type range in size from about 100 to 1.000 short tons per day capacity.

Plant Classification 1.4

Source and the products are almost the same as type 1.3.

Typical operating characteristics of these plants when operating at design conditions are given below for various feedstocks:

Feedstock	SO_2 in converter feed, mol %	Conversion SO_2 to SO_3,%
H_2S	6.5 to 7.5	95 to 98
Pyrites	6.5 to 7.5	95 to 98
Acid sludge	6 to 8	95 to 98
Copper converter gas	3 to 7	94 to 98
Roaster gas	5 to 7	95 to 98

Characteristics of the tail gas emissions from these plants may be expected to fall in the following ranges :

Feedstock	Maximum rate SCF/ton of acid(as 100 % acid)	SO_2content ppm	Acid mist,mg/SCF	
			producing 99 %acid	producing oleum
H_2S	99.000	1500 to 4000	2 to 20	5 to 50
pyrites	108,000	1500 to 4000	2 to 20	5 to 50
Acid sludge	117,500	1500 to 5000	2 to 20	5 to 50
Copper converter gas	184,000	2000 to 7000	2 to 20	5 to 50
Roaster gas	143,000	1000 to 4000	2 to 20	5 to 50

Sulfur losses per ton of acid produced (as 100 % acid) are as follows at design conditions :

	sulfur loss, tons		
	As SO_2	As acid mist	
Feedstock		Producing 99 % acid	Producing oleum
H_2S	0.007 to 0.017	0.002 max	0.005 max
pyrites	0.007 to 0.017	0.002 max	0.006 max
acid sludge	0.007 to 0.017	0.003 max	0.006 max
copper converter gas	0.014 to 0.021	0.004 max	0.010 max
roaster gas	0.007 to 0.017	0.003 max	0.008 max

The comments regarding steam, oleum production, emission control methods and economic calculations for classification 1.3 apply equally to class 1.4.

Plants in this classification range in capacity from about 150 to 1,600 tons per day.

5.3. Sulfuric Acid from Gypsum (natural gypsum, anhydrite and residual calcium sulfate) (Fig.8)

5.3.1. Sulfuric Acid from Natural Gypsum:

Rising sulfur prices in recent years have led to a search for alternative raw materials for making sulfuric acid. The latter is produced by catalytically oxidizing sulfur dioxide traditionally obtained by burning elemental sulfur or by roasting iron pyrites (impure Fe).

A solution to the shortage of elemental sulfur is available to companies having ready access to calcium sulfate either as deposits of anhydrite rock, or as by product gypsum from making **wet** phosphoric acid. It lies in the cement/sulfuric acid process.

In this process calcium sulfate is used in place of carbonate as a source of the calcium oxide component in cement. The sulfurdioxide required for sulfuric acid manufacture is produced when the calcium sulfate is processed in the cement kiln.

The products from the process are Portland cement and sulfuric acid in any of its normal commercial forms such as 98 %, 94 %, oleum or liquid sulfur trioxide. The acid is equivalent to the normal commercial grades and can be used for most purposes except possibly when specifications on nitrogen content are particularly severe. The cement clinker meets all the normal specifications of Portlant cement.

There are such plants at seven different works in Austria, East Germany, Poland, and the United Kingdom. All the operators of these plants are primarily chemical manufacturers who presumably regard the sulfuric acid as the main product and the cement as the by-product.

The origin of the process can be traced to Germany where plants were built during World War I to combat the shortage of sulfur. Manufacture of sulfuric acid from natural gypsum or anhydrite together with cement clinker began in 1916 in Leverkusen. Nowadays, it bears great importance as regards to the benefit of residual calcium sulfate from the wet process of raw phosphate.

It was not until the early 1920's that the operators overcame the major difficulties and the process was at all satisfactory. In 1929 one of the founder members of ICI commenced work on a single kiln plant at Billingham. After an extended commissioning period during which the company solved the operational difficulties with some co-operation from IG-Farben it installed a second kiln in 1932.

Although most of the operational difficulties as regards keeping the plant on line and ensuring a steady supply of sulfur dioxide gas to the acid plant had been solved, the quality of clinker was not as high or as consistent as possible. A further extensive development program in the early 1940 s eventually resulted in the production of unsatisfactory clinker dropping below 1 percent.

The application of gypsum-sulfuric acid process in fertilizer plants makes 90 % recovery of sulfuric acid possible. The effect of qualities of by-product gypsum and the other components on the cement quality is under investigation. The continuous utilization of residual gypsum makes the sulfuric acid--cement method more attractive. This method provides the arrangement of fertilizer composition by the proper ratio of gypsum and sulfuric acid. The removal of residual gypsum results in decreasing the environmental pollution.

Although all the processes in use are basically similar, differences occur in such features as the methods of preparing and blending the feed, the kiln design, the cooling of the cinder, and the dedusting and cooling of the kiln gases.

Ring formation can be a serious problem as in conventional cement kilns although there are probably more causes of ring formation in the cement--sulfuric acid process.

One of the principal items which licensors of the process sell is operator training and assistance: even the most experienced burner on normal cement kilns would find much of his accumulated know--how and experience of little value in the operation of a cement-sulfuric acid plant.

The raw materials for the process comprise calcium sulfate, preferably in the form of anhydrite, and a source or sources of silica, alumina, and iron. The choice of these auxiliary raw materials depends on the local circumstances. Their cost is usually low and the primary requisites are adequate supplies of material of as constant a composition as possible. The objectionable purities are similar to those in normal cement manufacture and one of the most important is magnesia since in excess it leads to cement which is unsound.

The overall reaction in gypsum-sulfuric acid process:

$$2CaSO_4 + C(coke) \longrightarrow 2CaO + 2SO_2 + CO_2 \qquad (1)$$

whereas in the conventional cement process calcination takes place as :

$$CaCO_3 \xrightarrow[760\ mmHg]{900^{o}C} CaO + CO_2$$

But, the dissociation of calcium sulfate takes places as :

$$CaSO_4 \longrightarrow CaO + SO_3$$

$$\underline{SO_3 \longrightarrow SO_2 + 1/2\ O_2}$$

$$CaSO_4 \xrightarrow[60\ mmHg]{1960^{o}C} CaO + SO_2 + 1/2\ O_2$$

with a great dissociation enthalpy.

Raw meal is fed into the kiln where the products of combustion of the fuel heat countercurrently. The function of the first and usually the longest section of the kiln is to remove the last trace of water and to pre-heat the raw meal before it enters the reduction zone.

In this zone, which extents from a temperature of about 700° to 1000°C, the carbon reduces part of the calcium sulfate to calcium sulfide, being itself oxidized to carbon dioxide:

$$\mathrm{CaSO_4 + 4CO \longrightarrow CaS + 4CO_2}$$

$$\underline{\mathrm{2CO_2 + 2C \longrightarrow 4CO}}$$

$$\mathrm{CaSO_4 + 4C \longrightarrow CaS + 4CO_2} \qquad (2)$$

For the reduction to begin coke is added; 20 % in excess, carbon monoxide forms as an intermediate. Separately pre-heated coal and calcuim sulfate in an oxygenless medium cause another reduction reaction.

In the next section of the kiln, the temperature range of which extents from 1000°C to 1200°C, the calcium sulfide formed reacts with the rest of the calcium sulfate to give sulfurdioxide and calcium oxide:

$$\mathrm{3CaSO_4 + CaS \longrightarrow 4CaO + 4SO_2} \qquad (3)$$

This reaction starts at 900°C and SO_2 is evolved at 1156°C and 760 mm Hg.

The latter immediately starts to combine with the acidic oxides present. By the addition of SiO_2, Al_2O_3 and Fe_2O_3 the reaction temperature is decreased. The side reactions are:

$$CaS + 2SO_2 \longrightarrow CaSO_4 + S_2 \qquad (4)$$

$$4CaO + 6SO_2 \longrightarrow 4CaSO_4 + S_2 \qquad (5)$$

$$4CaS + 2SO_2 \longrightarrow 4CaO + 3S_2 \qquad (6)$$

If the kiln atmosphere is strongly reducing, the reactions 4,5,6 occur giving the undesired elemental sulfur. The product calcium oxide from reaction 3, with the kiln-dust containing SiO_2, Al_2O_3, $Fe_2\ O_3$ gives the clinker minerals in the sinterzone.

In the final section of the kiln, the temperature range of which extends from about 1200° to 1400°C, clinkering occurs ; part of the mixture melts and the liquid phase present greatly assists the final formation of the cement compounds. The clinker is then cooled by direct contact with the secondary air to the kiln which is at the same time pre-heated.

Pulverized coal or oil is normally employed as fuel for the kiln, although gas may be used. Here one would normally make the choice on economic grounds, although oil or gas have the advantages that they introduce very little in the way of other components into the kiln. In contrast, the ash from pulverized coal goes into the clinker so that account has to taken of this in blending the raw meal.

The gases from the kiln usually contain 9 to 10 % of sulfurdioxide and 20 % carbondioxide by volume with only traces of oxygen. A small quantity of carbonmonoxide and free sulfur vapor is also present and this has to be oxidized by adding some excess air. This may be added either part way along the kiln or in the smoke box at the end.

The gases from the kiln then pass through a hot gas dedusting system comprising cyclones or electrostatic precipitators or both to the washing system for cooling and purification before entering the sulfuric acid plant.

This section of the plant follows normal sulfuric acid techniques and no special comment is called for. However, there are certain differences from say a pyrites burning installation.

The gas from the kiln is appreciably weaker in sulfurdioxide than that obtained from burning iron pyrites and by the time suficient excess air has been added to allow for efficient oxidation to sulfurtrioxide in the sulfuric acid plant, the gas concentration is between 5 and 6.5 % SO_2, as opposed to the 7 % which would be expected on a pyrites burning plant. This means that the acid plant has to be larger and consequently more expensive.

A certain amount of atmospheric nitrogen is fixed in the kiln and this gives use to a very misty effluent gas from the acid plant. This gas usually has to be treated in electrostatic precipitators to minimize atmospheric pollution.

Sulfurdioxide from reaction (3) is sent to the sulfuric acid unit with the other gases. This gas contains some fluoride compounds coming from residual gypsum (SiF_4,HF). In the cement kiln these compounds in gaseous form react as such :

$$CaF_2 + H_2O \longrightarrow CaO + 2HF$$

$$4HF + SiO_2 \longrightarrow SiF_4 + 2H_2O$$

$$Na_2SiF_6 \longrightarrow 2NaF + SiF_4$$

These gaseous F-compounds damage the vanadium catalyst necessary for the sulfurdioxide oxidation and the kieselguhr carrier forming vanadium fluoride. Therefore these gases should be removed before entering the catalyst chamber.

The product clinker corresponds to normal portland cement of standard DIN 1164, and can be easily converted to Ö-Norm B 3310. Sulfuric acid composition results as :

H_2SO_4	98 %
SO_2	0.01 %
Fe	0.0035 %

Figure 9 shows the dependence of sulfuric acid production cost on capacity and cement credit. In calculating the product costs the 1972 prices in Western Germany are used.

Two plants are operating with this method in Western Germany of capacities 80,000-105,000 tons per year monohydrate now. In such a plant, in addition to sulfuric acid, cement clinker is produced in equal amounts .

The largest plants in current operation produces 80,000 to 100,000 tons per year from a single kiln. There would certainly be no difficulty in designing a single kiln to operate at 160,000 tons per year and current technology indicates that a single-stream plant of about 500,000 tons per year would be feasible.

Considerably larger capacities than this already exists in conventional kilns. However the output of cement from the cement-sulfuric acid kiln is considerably lower than for a conventional cement kiln of the same dimensions. This is partly due to the greater heat requirements for the process. (88, 118)

5.3.2. Sulfuric Acid From By-Product Gypsum :

The anhydrite kiln process has been adapted for the production of SO_2-containing gas and Portlant cement clinker from gypsum made as a by-product of phosphoric acid manufacture. Some of the fluorine present in the by-product gypsum enters the SO_2-containing gas, but this fluourine which would poison the vanadium oxidation catalyst, can be removed during the gas cleaning operations and there are therefore no problems in the use of this gas for sulfuric acid manufacture. The limits of impurities, especially P_2O_5 and F in by-product gypsum, for the production of high-quality cement are not given in the literature, but published information suggests that cement can be made which meets BS 12:1958, but leaves it uncertain whether this cement would satisfy those users for whom high-early strength is needed. A potential user of by-product gypsum in a kiln-acid plant should ascertain the uses to which the cement would be put and obtain explicit guaranties that the cement made from by-product gypsum would meet requirements.

Gypsum produced as a by-product of phosphoric acid manufacture is usually dumped. The composition of the gypsum is therefore of little importance to the operator of a phosphoric acid plant, although he will usually wish to minimize the P_2O_5 lost in it.

There may, however, be occasions when he is prepared to accept a higher P_2O_5 loss in the gypsum, for example, to increase phosphatic acid output. If the by-product gypsum is to be fed to a kiln-acid plant, the phosphoric acid plant operator will have to produce his by-product gypsum to a specification and this may interfere with the way in which he would otherwise wish to run the phosphoric acid plant.

If gypsum is to be produced to a specification in a new phosphoric acid plant, the plant should be carefully designed to convert as much as possible of the P_2O_5 in the phosphate rock into water-soluble P_2O_5, thus minimizing the water-insoluble P_2O_5 in the gypsum. The amount of water-soluble P_2O_5 in the gypsum will depend on the washing efficiency of the gypsum filters. These also determine the free moisture content of the gypsum. The filters should therefore be chosen to produce a gypsum filter cake with the minimum practicable amount of water-soluble P_2O_5 and the lowest possible free water content.

The gypsum specification may also limit the F content. This will vary with the type of phosphate rock used. For example, a rock high in SiO_2 and F will produce fluosilicic acid the sodium fluosilicate up to the limit of its solubility will go out in the phosphoric acid, giving gypsum which is relatively low in F. On the other hand, phosphate rock high in F, but low in SiO_2 will produce gypsum with a relatively high F content. The purchaser of a phosphoric acid plant should ascertain if his choice of phosphate rocks is likely to be restricted by the specified F content of the by-product gypsum because he might find such a restriction to be commercially undesirable..

It is possible to obtain Portlant cement of standard quality from clinker containing 3 to 5 percent of P_2O_5 which has been made from raw meal with a limited lime content. The ratio of C_3S/C_2S in such clinker is 1.2-1.4 : 1. As the P_2O_5 content of clinker increases from 0 to 15 per cent of P_2O_5 , C_3S progressively disappears to give free CaO and C_2S which form solid solutions with C_3P. These changes are already apparent to a considerable degree at 3 per cent of P_2O_5 in clinker and clinker containing 15 per cent of P_2O_5 contains scarcely any of the usual minerals of Portlant cement clinker.

The addition of small amounts of fluorine as CaF_2 in the presence of P_2O_5 (3-5 percent of P_2O_5 in the clinker) stabilizes C_3S and enables cement to be produced which contains 50-60 per cent of C_3S with no free lime.

The compressive strengths of cement made from clinker containing 3 per cent of P_2O_5 are similar to those of plant-produced cements.

The amount of P_2O_5 that can be tolerated in raw meal made from by-product gypsum is limited. The stabilizing action of CaF_2 on the C_3S in P_2O_5 containing clinker requires the incorporation of small amounts only of CaF_2 in raw meal. It would seem to follow from this that the absolute amount of CaF_2 in raw meal, and/or the P_2O_5/CaF_2 ratio in it, must be carefully controlled.

The results of full-scale trials have not been published in detail because the information obtained from there is largely regarded as the confidential know-how of the companies concerned.

The main difference when the process is operated on by-product gypsum instead of anhydrite lies in the treatment of the by-product gypsum before it is incorporated into the raw meal. By-product gypsum is usually finely divided and therefore does not normally need grinding. It is partially or completely dehydrated, as with mineral gypsum, and taken to storage bunkers. By-product gypsum losses some fluorine during dehydration and wash towers are installed after the dust cyclones to prevent the discharge of fluorine to atmosphere. The other constituents of raw meal are dried, ground separately and taken to ~~separate storage bunkers. The components~~ of raw meal are withdrawn from these storage bunkers in the correct proportions, mixed and fed to the kiln through raw meal storage bunkers. Alternatively, the ingredients of raw meal other than by-product gypsum are mixed and subsequently blended with the dehydrated gypsum. The kiln firing temperature is slightly lower than with anhydrite, presumably due to the fluxing action of CaF_2 in the raw meal.

As a result of the tests they made, Polimex is in a position to supply know-how for a plant to make sulfuric acid and clinker from by-product gypsum, alone or mixed with anhydrite. Polimex in its "Preliminary Offer for the Production of Sulfuric Acid and Cement Utilizing Phospho-Gypsum as the Raw Material" regards plant to produce 100,000 tons of sulfuric acid per year as the minimum economic size.

V.E.B. Chemiewerk, Coswig, German Democratic Republic, have also done full-scale tests on the use of by-product gypsum in a kiln-acid plant and developed a process that is said to enable sulfuric acid and high-quality cement to be made from by-product gypsum. The efficiency of conversion of calcium sulfate in the by-product gypsum to sulfuric acid is 80 percent and the ratio clinker to H_2SO_4 about 0.93. The effect of P_2O_5 or CaF_2 on clinker quality is obviously part of the know-how which operators are unwilling to disclose.

The key to the successful operation of the process is said to be in the control of the kiln operating conditions because by-product gypsum is more reactive than mineral calcium sulfates. Control of raw meal composition and kiln operating conditions are thus even more important when using by-product gypsum than when working with mineral calcium sulfate. (117)

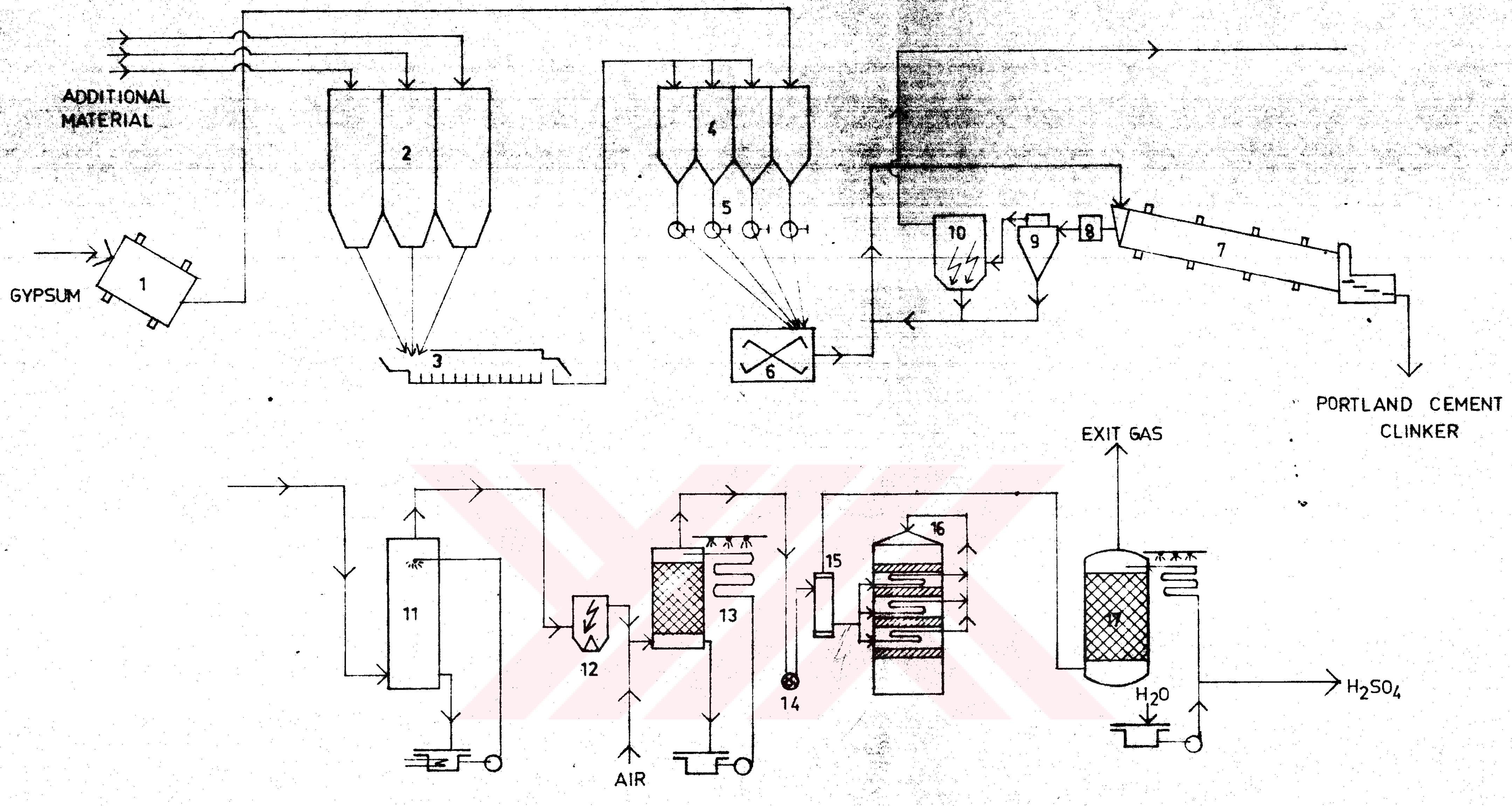

FIGURE 8: FLOWSHEET FOR PRODUCTION OF SULFURIC ACID AND CEMENT FROM BY-PRODUCT GYPSUM (81)

1. GYPSUM DRIER
2. AUXILIARY MATERIALS SILOS
3. GRINDER FOR AUXILIARY MATERIALS
4. RAW MATERIAL SILOS
5. WEIGHING
6. MIXER
7. ROTARY KILN
8. CLINKER DRYER
9. GROUP OF CYCLONES
10. ELECTROFILTER
11. WASHING TOWER
12. WET FILTER
13. DRYING TOWER
14. AIR COMPRESSOR TO ROTARY KILN
15. HEAT EXCHANGER
16. CONTACT CHAMBER
17. ABSORPTION TOWER

CHAPTER 6

ENVIRONMENTAL CONTROL

6.1. Environmental Control in Sulfuric Acid Manufacture

Atmospheric emissions from sulfuric acid plants vary, both in quantity and composition, depending upon the process, the mode of operation of the plant and the condition of the plant. All emissions which are of any concern, however, emanate from one source-tail gas stack of the plant, regardless of size, type, or acid grade produced. Emissions of objectional sulfur compounds from sulfuric acid plants result from either incomplete conversion of the sulfur source to sulfuric acid, or from carry over of acid mist and droplets formed or entrained in the tail gas. The quantity of sulfurdioxide present in the tail gas is a very small fraction of the total flow, usually less than 1 %.

Environmental problems arising from sulfuric acid plants are not due to the total quantity of sulfurdioxide and acid mist which they discharge to the atmosphere because these are relatively small.

Problems are generally localized and caused by relatively high percentages of sulfurdioxide and/or acid mist (up to 1/2 %) combined with relatively low tail-gas temperatures and other short stacks which result in poor dispersion. The result is ground level concentrations of sulfurdioxide and mist which may exceed desirable limits in the immediate vicinity of a plant, especially during adverse atmospheric conditions.

The typical design conversion efficiency of recently built sulfuric acid plants is 98 %. If this design efficiency were maintained the exit gas concentrations of sulfurdioxide would be 2000 ppm or less. Frequently emissions of 3000 to 4000 ppm and more are encountered in actual practice. Control regulations of 500 ppm sulfurdioxide being discussed in some areas of the United States, which indicates a considerable gap between this practice and proposed control levels.

Existing sulfuric acid plants can reduce their emissions somewhat by modifying their operating conditions with little capital expenditures, but this control is limited to about 2000 ppm of sulfurdioxide. Present technology can achieve a control effectiveness of 500 ppm of sulfurdioxide via the dual absorption route, and excellent acid mist control in the order of 0.1 mg/scf.

Cost of emission control varies widely with plant capacity, type of control system and other factors. Cost of less than 500 ppm sulfurdioxide control for a 250 tpd contact plant varies from about $ 0.75 to over $ 3 per ton of acid. Mist control costs vary from $ 0.02 to $ 0.35 per ton of acid. Control cost is lower for large plants.

Many systems for emission control for sulfuric acid plants and other stationary sources have appeared in the literature, a few of which are in commercial operation. Some have been extensively tested in the laboratory, and in a pilot scale unit, but the majority, tested only in part, are patents untested on a continuous basis or actual conditions, or represent undeveloped ideas. Since sulfurdioxide and mist control in all cases represents an addition to the cost of producing acid, there has been no commercial incentive to develop control processes or devices beyond the economic use of raw materials and the requirements of social nature imposed by local government authorities. The majority of commercially operating control systems have been in the area of mechanical devices for acid mist control, since the presence of acid mist is the easiest to detect and produces direct effects which tend to evoke immediate complaints from owners of adjacent properties.

Mist control is also relatively inexpensive.

In order to measure the capabilities of various systems it is first necessary to establish criteria by which the various systems will be compared. For measurement of overall capability of a system or process, the term "control effectiveness" has been used, which may be defined as the total outlet concentration of sulfur expressed as ppm of sulfurdioxide, regardless of the inlet concentration to the control system. For mist control only the measurement is normally given as mg/scf.

Emission control systems were judged for feasibility by considering a number of factors including stage of process development, applicability to a significant number of existing acid plants, potential for good control effectiveness for sulfurdioxide, acid mist or both, estimated on stream reliability, marketability of by-product (if any), and overall estimated value compared to other systems, with similar chemistry or processing features. Those systems selected for further analysis were evaluated at sulfurdioxide or overall control effectiveness levels of 2000 ppm, 500 ppm and 100 ppm or less. 2000 is chosen since it represents the approximate levels which can be achieved by most modern

modern plants with careful operation and minimum expenditure. The 500 ppm level represents the aim of many of the pollution control regulations which are under consideration in the United States. The 100 ppm level was chosen since it represents a desirable level below which SO_2 ceases to be much of a problem, or which may be the long range requirement in the future.

The concentration of sulfurdioxide in cleaned gas brings about concentrations of sulfurdioxide in the ambient air at ground level in proportion to the weight per unit of time being emitted from the stack. The contaminant concentration at ground level is also governed by distance from source to point of measurement, effective stack height, plus geographic and meteorological factors. The effective stack height and distance from source should be such that under the more unfavorable meteorological conditions the short durationed peak sulfurdioxide concentrations should not exceed 1 ppm as noted by Drs.Y.L. Whittenberger and R.N. Frank," Human Exposures to Sulfur Dioxide", Archives of Environmental Health, Vol. 7, No.2, August 1963. A stack emission of 100 ppm from most acid plants will generally result in an ambient air quality at ground level to satisfy this condition. For a specific plant the emission would have to be calculated using stack height and other local factors. A study of the effects of all the variables involved in the relationship between ground level concentration and stack emission level may be desirable.

Processes which control sulfurdioxide emission may or may not provide a measure of control for acid mist as well. It is desirable to reduce acid mist emission to remove the visible plume from an acid plant stack. All such plants will discharge some acid mist to the atmosphere, and sulfurtrioxide will combine with the moisture in the air to form additional acid mist. Most devices used and which are incorporated on the stacks of many existing plants will remove nearly 100 % of all mist particles of 3 microns or larger. The problem lies with that portion of the mist which is droplets of less than 3 microns. By removing all particles less then 3 microns the mist emission can generally be reduced to 2 to 3 mg/scf for plants producing upto 99 % sulfuric acid. For oleum plants, however, removal of particles less than 3 microns reduces mist emission, but not nearly as effectively because the mist discharged from an oleum plant stack contains a much greater percentage of finer droplets.

The relationship between the acid mist and sulfur dioxide concentration in the cleaned gas will be the same after dilution as at the stack, since mist particles are small enough to behave as a gas, especially in the smaller sizes. With the toxicity of acid mist at least 4 times as great as sulfurdioxide emission of acid mist should be in the order of 3.0 mg/scf (max)(25 ppm) to avoid a contamination problem. (8)

Three general methods of mitigating the discharge of sulfuric acid plants have been adopted:

6.1.1 Increased Stack Height:

Increasing the stack height does not reduce the total pollution but only spreads it over greater area where it may be less obnoxious and harmful. The proper approach, and that now being adopted in many places, is to determine the stack height required for reasonable ground level concentration of the sulfurdioxide after other methods of reducing the total emission have been applied.

6.1.2 Modification to the Design of the Acid Plant:

Unquestionably the proper way to reduce pollution is to convert more of the sulfurdioxide to acid. There are three ways that this can be done which have been or are being investigated currentlyas described below:

6.1.2.1 A Low Temperature Catalyst:

Most catalysts available to the industry are active at about 440°C. With an 8 % sulfurdioxide feed gas, consideration of thermodynamic equilibrium limit the conversion obtainable at this temperature to 98.5 %. If a catalyst would be developed which would be active at 300°, the conversion might be increased to 99.97 %.

6.1.2.2 The Double Absorption Process :

If after some of the sulfurdioxide present is converted to sulfur trioxide, this sulfur trioxide is removed (by absorption) and the gas returned to the converter, the equilibrium conditions are changed and a greater proportion of the sulfurdioxide can be converted. This process was first used in Germany in 1964 and although it initially spread rather slowly, it is now being widely adopted. Most plants now being designed or built in industrial countries are adopting this method which is described in chapter 5.2.4.

6.1.2.3 The Pressure Process:

Traditionally, sulfuric acid plants operate at close to atmospheric pressure and, although the trend is towards higher pressure drop through the plant which raises the pressure at the converter slightly, this is not enough to affect equilibrium considerations.

However, a substantial increase in operating pressure would not only increase the equilibrium convertion of sulfurdioxide to sulfurtrioxide but would assist with the absorption of sulfurtrioxide. Some patents have been recently published and a plant using this principle is now under construction in France.

After drying, air is compressed to 60-100 psig and sulfur is burned in this air under pressure. The hot gas is cooled in a boiler to converter temperatures and passes through a multistage converter with inter-stage coolers before final cooling and absorption of sulfurtrioxide under pressure. Present indications are that in plants of the capacities now being built, a pressure plant would be more expensive than a dual absorption plant but at very large capacities, the reduction in size of equipment possible with a pressure plant would make it economically attractive.

6.1.3 Tail Gas Treatment :

Instead of attempting to improve the dispersion of the sulfurdioxide vented, or to improve the conversion, it is also possible to remove the sulfurdioxide from the stack gas by after-treatment. A very large number of processes have been proposed over the last half century and interest has been considerably stimulated by studies of methods for removing sulfurdioxide from power plant stack gas. Broadly these processes may be divided into three catagories as described below:

6.1.3.1 Absorption with By-Product :

The usefulness of such a process depends on the value of the by-product or the difficulty of disposing of it. Unfortunately, most by-products are of no commercial value and may themselves result in a pollution problem (e.g. lime scrubbing to produce calcium sulfite; soda ash scrubbing to produce sodium sulfate).

Most of the earlier plants used single stage scrubbing to reduce the sulfurdioxide concentration to about 500-800 ppm. The current generation of plants uses two stages of scrubbing and sometimes a third washing stage to recover ammonia. In any case, the scrubbing solution is a mixture of ammonium sulfide and bisulfite with a weaker, more alkaline solution in the second stage than in the first. This weaker solution is used as make up to the first stage and a bleed of product solution is taken from this stage for recovery of sulfurdioxide. Provisions is made to add ammonia to both stages so that the pH in each stage may be independently controlled.

6.1.3.2. Absorption with Regeneration :

These processes (many of which have been developed) always require heat for regeneration of the solution. Many of the processes developed for power plant stack treatment are in this category and two such processes have received considerable publicity and are in advanced stage of development. A sodium sulfide-bisulfite process is in operation on a sulfuric acid plant in the United States. A magnesium oxide scrubbing process with regenaration of sulfurdioxide, developed by Chemical Construction Corporation, is being erected in New England for a power plant.

6.1.3.3 Adsorption on Solid Adsorbent :

Although no process using solid adsorbent has yet been installed, several manufacturers of resin and molecular sieves are known to be investigating the problem. In many cases, adsorbents of this type will remove not only sulfurdioxide but any remaining sulfurtrioxide, acid vapor and acid mist. It may be more difficult to regenerate these sulfate forming compounds than the sulfurdioxide. Solid adsorbents have the capability of reaching very low sulfur dioxide concentrations (10-50 ppm have been mentioned) but there appears to be a considerable amount of development work involved. (47).

6.2. Economics of Control Systems :

As for any other process or device, technical considerations for selection of an acid plant emission system will include: technical capability to achieve the required control effectiveness, by actual demontration preferably, on-stream reliability, simplicity, flexibility to handle varying concentrations, also to be modified if necessary to comply with more stringent regulation in the future. Of lesser importance are the following. Installation will not interfere with acid plant operation. No unfamiliar operations are required. No new disposal problems are introduced, either of waste material or salable by-products. Small space requirements are considered.

An ideal system, in addition to all of the above would require minimum operating cost and be applicable to all types of acid plants. At present, no such system has been developed. It should be emphasized that the criteria for selection of a control system for application to a sulfuric acid plant are not necessarily the same as for other applications where gas flows, compositions and temperatures are different and whose general operation are of a different nature, such as power plants and the like.

Control cost is determined by calculating the cost of producing one ton of acid in a plant with a given control system, and subtracting the cost of producing one ton of acid in the same plant without the control system, all on an annual basis, and taking into account the increased production of the more efficient plant with the control system.

Cost for several systems on Tables 48, 49,50,51, 52 were estimated for the same set of conditions so that results would be comparable. As the basic reference point, a nominal plant capacity (which here means plant capacity at normal operating conditions before inclusion of a control system) was selected at 250 ST/D.

Most processes fit three different classes of acid plants, 1.1, 1.2 and 1.4 as applicable, under the following flow rates and emission levels.

Class	Emission Level (ppm)	Tail Gas Flowrate (CF)
1.1	5,000	18,700
1.2	2,500	18,700
1.2	4,000	18,700
1.4	3,200	29,200

For the design of the recovery process the tail gas was assumed to be discharged at 154°F in all cases.

In comparing the control systems; of the add-on dual absorption systems 1.2.2 (using furnace heat-see Appendix G) seems to offer sulfurdioxide control at minimum cost, especially if the base plant is capable of additional acid capacity as a result of inclusion of 1.2.2. This is true over the entire existing capacity range for single units. For tail gas recovery processes, however, the selection is not as clear cut. Generally, for small plants the simplest system, 2.3.3 (lime absorption of sulfur dioxide) and 2.2.29 (resin absorption of sulfur dioxide) produce minimum control cost. For larger plants, 2.2.6 (magnesium oxide absorption) and 2.2.14 (methylamine sulfite-bisulfite absorption) appear most attractive. There is an intermediate area where the control cost for these four above mentioned systems are approximately equal.

Mist control systems, like dual absorption process, control only a part of the total emission problem of contact acid plants. They can be applied to any type of acid plant, and a majority of operating plants today include some type of mist control device. Regulations governing mist concentrations at ground level vary widely, and suitability of systems should be determined on an individual basis.

The principal cause for variation in control cost in using these devices is not control effectiveness, inlet concentration or type of plant, but whether the plant is new or existing. For most systems there is a market saving when the system is provided initial over the cost of adding one later. The exceptions are 3.2.1 (electrostatic precipitation) and 3.3.1 (mist removal with venturi scrubber) which are normally external units not incorporated with the absorption tower in any case.

More detailed information on effluent control in sulfuric acid plants, about processes and costs can be found in (133).

Since sulfuric acid manufacture is an old art, the major developments of current concern are pollution control and pollution control economics. It is not likely that there is any contact acid plant in the United States to which a satisfactory emission control system could not be applied. It is doubtful, however, that all plants could be operated economically with control systems, and such decision would necessarily have to be made on an individual basis. If some plants are forced to close because the cost of control was too high, older, smaller plants with restricted choice as to possible control methods would probably be most affected.

TABLE 49 : Control Costs For Various Tail Gas Recovery Processes Applied to Various Types, Capacities and Efficiencies of Acid Plants for Sulfur Dioxide, Sulfur Trioxide and Mist Control (133)

	Emission Level					
Process	In (ppm)	Out	50tpd	250tpd	750tpd	1,500tpd
Sodium Carbonate Absorption	5,000	250	$	$ 3.13	$	$
"	4,000	200		3.05		
Sodium Carbonate Absorption						
Magnesium Oxide Absorption (x)	5,000	250		2.57		
"	4,000	200	8.61	2.37	1.05	0.68
"	2,500	125		2.36		
"	2,000	100		2.35		
"	3,200	160		2.70		
MgO Absorption	5,000	250		2.71		
"	4,000	200	8.82	2.51	1.18	0.80
"	2,500	125	8,70	2.51	1.15	0.78
"	3,200	160		2.92		
Potassium Sulfite Bisulfite Absorption	5,000	250		2.84		
"	4,000	200		2.73		
"	3,200	160		2.35		

Table 49: Cont'd

Process	Emission Level In (ppm)	Emission Level Out	50tpd	250 tpd	750tpd	1,500tpd
Methylammonium Sulfite-Bisulfite Absorption	5,000	250		1.98		
"	4,000	200	8.10	1.88	1.03	0.78
"	3,200	160		2.58		
Aluminium Sulfate Absorption	5,000	500		2.87		
"	5,000	250		2.87		
"	4,000	200		2.96		
Resin Absorption	5,000	-0-		1.50		
"	4,000	-0-	4.15	1.63	1.08	0.86
Lime Absorption	5,000	250		2.33		
"	4,000	200	8.00	2.14	1.33	0.94
"	3,200	160		2.48		
Ammonium Sulfite-Bisulfite Absorption	5,000	250		2.63		
"	4,000	200		2.52		
"	3,200	160		3.05		
Sulfuric Acid Lime 2 Stage Absorption	5,000	250		3.50		
"	4,000	200		3.33		
"	3,200	160		3.76		

(x) SO_2 emission control only.

TABLE 50 : Approximate Capital Investment Requirements for Various Acid Mist Control Systems ($) (133)

	New Plants				Existing Plants			
	50 T/D	250T/D	750T/D	1,500T/D	50 T/D	250T/D	750T/D	1,500T/D
Control System	3,750 CF	18,700	56,000	112,000	3,750	18,700	56,000	112,000
Dual Mesh Pads Sep.	10,000	20,000	28,000	38,900	13,000	25,000	35,000	48,000
Tubular Fibre Type Sep.	55,000	70,000	105,000	170,000	78,000	100,000	150,000	240,000
Panel Fibre Type Sep.	14,000	23,000	55,000	95,000	27,000	44,000	105,000	170,000
Electrostatic Precip.	60,000	85,000	105,000	200,000	60,000	85,000	105,000	200,000
Venturi Scrubber		70,000						

NOTE: Size and cost depends upon tail gas flow rate.

Costs are given for class 1.2 sulfur burning plants.

Adjustments proportional to gas flow must be made for various wet gas plants.

TABLE 51 : CONTROL COST FOR VARIOUS MIST CONTROL SYSTEMS APPLIED TO VARIOUS TYPES OF ACID PLANTS ($) (133)

Process	Non-oleum Plants						Oleum Plants					
	Existing Plants			New Plants			Existing Plants			New Plants		
	50 T/D	250 T/D	750 T/D	50 T/D	250 T/D	750 T/D	50 T/D	250 T/D	750 T/D	50 T/D	250 T/D	750 T/D
Dual Pad Mist Separators												
5,000 ppm	0.10	0.08						0.06				
4,000 ppm	0.10	0.07	0.02					0.04				
3,200 ppm		0.11						0.05				
				0.10	0.06	0.02					N.A.	
Tubular Type Mist Separators												
5,000 ppm		0.33										
4,000 ppm	1.25	0.33	0.17					0.28				
3,200 ppm		0.45										
Panel Type Mist Separators												
5,000 ppm		0.15										
4,000 ppm	0.45	0.13	0.10									
3,200 ppm		0.23										
Electrostatic Precipitation												
5,000 ppm		0.26										
4,000 ppm	1.05	0.25	0.22	1.05	0.25	0.22	0.90	0.22	0.19	0.90	0.22	0.19
3,200 ppm		0.33										
Mist Removal With Venturi Scrub.												
4,000 ppm		0.36										

TABLE 52 : COMPARISON OF ACID PRODUCTION COSTS FOR MULTI-UNIT PLANT WITH CONTROL SYSTEMS DUAL ABSORPTION AND MgO ABSORPTION (with 1970 prices) (133)

NOTE: Plant consists of 4 units; 2 class 1.1, 150 T/D each, 1 class 1.2, 300 T/D and 1 class 1.2, 600 T/D for a total daily production of 1,200 T/D.

Process	MgO Abs/Emission levels of 5000,2500 ppm	Dual Abs/Emission levels of 5000,2500 ppm
Nominal Capacity	1,200 T/D	1,200 T/D
Production Rate	1,254 T/D	1,250 T/D
Conversion Rate	99.775 %	99.5 %
Initial Investment	$ 6,215,000	$ 6,825,000
Book Value	3,295,000	3,905,000
Raw Material and Utilities		
Sulfur	$ 3,390,000	$ 3,390,000
Elec.Power	211,000	277,000
Cooling Water	124,200	144,000
Process Water	1,650	1,650
B.F.Water	28,900	23,700
Steam	-322,500	-260,000
Fuel Oil	150,300	
MgO	53,800	

TABLE 52 cont'd

Operating Expenses		
Labor	237,500	190,000
Supervision	63,300	63,300
Maintenance(4 %)	247,500	273,000
Overhead 70% of above	384,000	368,500
Indirect Costs		
Depreciation 10 %	576,500	683,000
Interest 7-1/2 %	[illegible]	
Taxes and Insurance (1-1/2 %)	93,200	102,300
Annual Operating Cost	$ 5,239,350	$ 5,256,450
T/Y Acid Production	413,300	412,000
Production Cost/T	$ 12,68	$ 12.76

CHAPTER 7

PLANT COSTS FOR SULFURIC ACID

7.1. Total Fixed Capital Investment and Production Costs for Different Sulfuric Acid Plants (153):

The production of sulfuric acid from brimstone or pyrites by fluidized bed processes seems to be more economical than from gypsum which is produced in considerable quantities as a by-product in the production of phosphoric acid by the mineral acidulation of phosphate rock.

TABLE 53: SULFURIC ACID PRODUCTION COSTS FOR VARIOUS RAW MATERIALS (US $ per ton) (1971) (153)

	Brimstone	Pyrites	Gypsum
Net Conversion cost	1.63	7.57	16.68
Raw Material cost	10.50	4.12	0.00
Total cost	12.13	11.69	16.68

These calculations have been based on an acid plant with a capacity of 400,000 tons per annum. In that case, it was estimated that (153) investments amount to :

for a brimstone-based plant	$ 4.0 million
for a pyrites-based plant	$ 11.3 million
for a gypsum-based plant	$ 16.8 million

The production cost for by-product gypsum -based plant for 1972 is plotted in Figure 9.

In the Table 54 for the Kent-ISU, Cement/Sulfuric Acid and Sulfur burning process, the costs are compared.

Lime-sulfuric acid (Kent-ISU) process, although not commercialized, can compete with the cement-sulfuric acid process, since the former's capital requirements are much lower than those of the latter. Moreover, this process could be of interest to sulfuric acid producers in countries which have plenty of anhydrite or gypsum feedstocks and no elemental sulfur. A great advantage of the process is that the by-product amount to only 0.6 ton of lime per ton of acid, while in the cement process the relation is 1 to 1. Furthermore, the lime produced is reactive, and therefore suitable for water and sewage treatment, for chemical neutralization and for soil stabilization and road building.

However, although certainly the lime as well as the cement processes avoid dependence on elemental sulfur, it must be pointed out that the sulfur-burning process is more advantageous as regards to capital costs and utility charges, which largely counterbalance the fact that sulfur costs twice as much as the anhydrite.

Table 55 shows the capital investment per ton of product for various sulfuric acid plants.

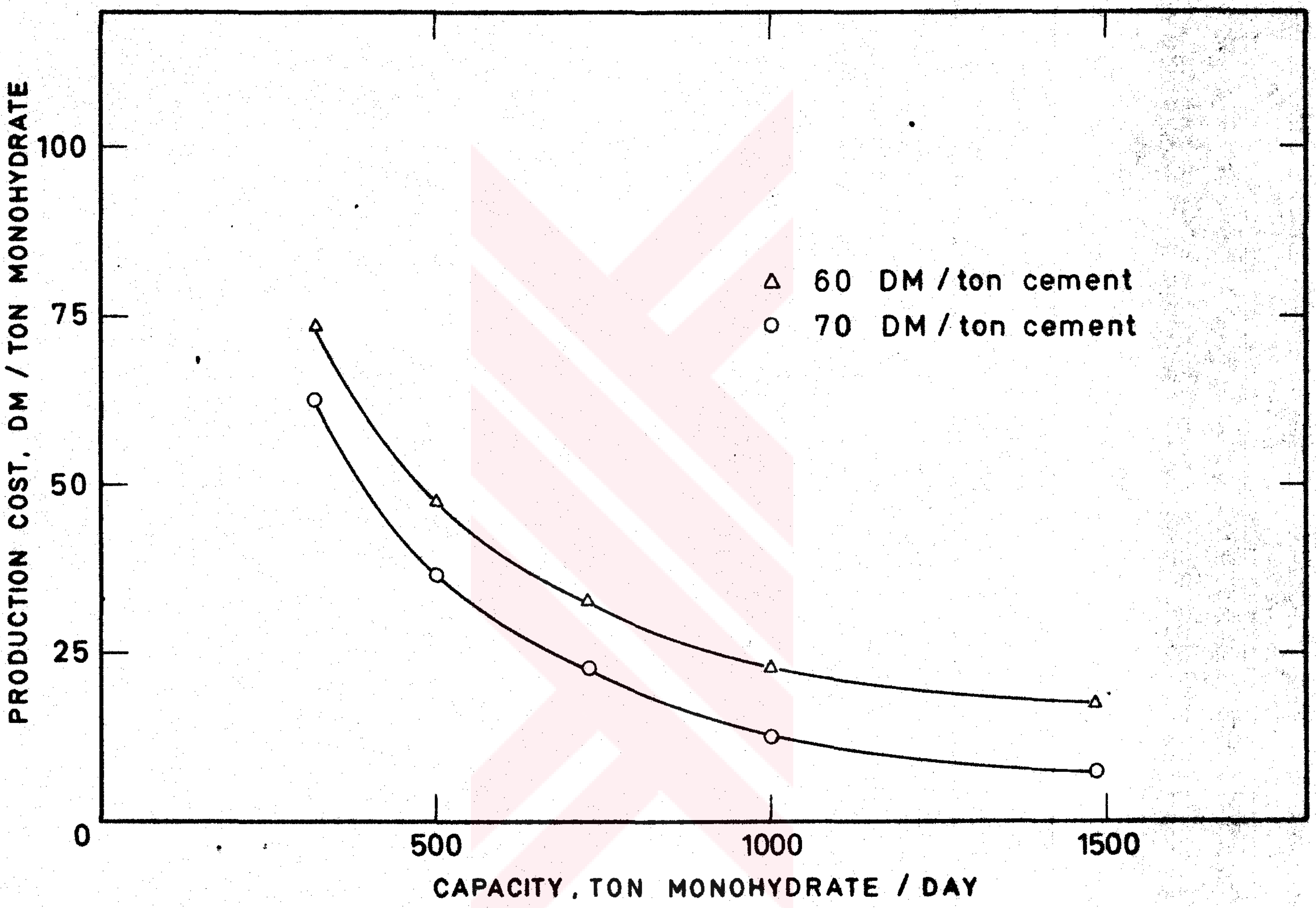

FIGURE 9: Production Cost in Cement – Sulfuric Acid Process (1973) (88)

TABLE 54: PRODUCTION COSTS FOR 1000 TONS/DAY (330,000 t/year) SULFURIC ACID PLANTS (1971) (153)

	Unit	Unit Cost $	Kent-ISU Cost, $/ton	Cement/Sulfuric Acid cost, $/ton	Sulfur burning cost, $/ton
Raw Materials					
Anhydrite	ton	3.0	4.5	4.8	-
Coke	ton	10.0	-	1.0	-
Sand	ton	1.2	-	0.2	-
Ash	ton	1.2	-	0.2	-
Sulfur	ton	30.0	-	-	9.0
			4.5	6.2	9.0
Utilities					
Electricity	kwh	0.012	0.96	1.80	0.10
Process water	ton	0.10	0.02	0.03	0.16
Cooling water	ton	0.005	0.32	0.35	0.17
Fuel (natural gas)	10^6kcal	1.6	3.10	2.80	-
			4.4	5.0	0.4
Labor and supervision			0.2	0.3	0.1
Maintenance			1.4	3.1	0.6
Depreciation and interest(20%)			5.5	12.1	2.5
Overheads (100% labor and maintenance)			1.6	3.4	0.7
	Subtotal		17.6	30.1	13.3
Less credits for					
Clinker	ton	8.4	-	8.4	-
Lime	ton	9.0	5.2	-	-
Steam	ton	1.2	-	-	1.2
Total Cost $/ton			12.4	21.7	12.1

TABLE 55 : CAPITAL INVESTMENTS FOR DIFFERENT SULFURIC ACID PLANTS (157)

Process	With 1950 prices capital investment per annual ton of plant capacity ($/ton)	With 1971 prices (converted)
1. Contact sulfuric acid from smeltergas	24.5	55.5
2. Contact sulfuric acid from sulfur	17	38.55
3. Sulfuric acid from anhydrite	72.5	164.3
4. Contact sulfuric acid from pyrites	36.25	82.5

Note: Capital investment = fixed capital + working capital; where working capital is around 10-15 % of fixed capital.

7.2. Cost Approximations for Different Plants in Turkey:

In order to come to a conclusion as how much it will cost to construct a factory (for factories) to meet the deficit in production of sulfuric acid, it is supposed to be helpfull to give some examples on the costs of various raw material based plants.

While comparing two cost figures, corrections for time and capacity are required.

It is a reasonable assumption that in chemicals investments 30 % of the project cost belong to construction works and 70 % to the equipment.

a) Without changing the capacity, the investment cost (fixed capital investment) at a different year can be calculated as follows:

$$M_2 = M_1 \left[\frac{x_2}{x_1} (0.30) + \frac{y_2}{y_1} (0.70) \right]$$

where;

M_2 = investment cost at year 2
M_1 = investment cost at year 1
x_2 = the construction cost index for year 2
y_2 = the machinery and equipment cost index for year 2.

b) For the same year, the investment cost for a different capacity can be calculated as follows:

$$\frac{M_1}{M_2} = \left(\frac{K_1}{K_2}\right)^{0.6}$$

Here, the capacities need to be at the optimum range.

For cost approximation purposes three examples are selected as a guide for raw materials appearing important in Turkey's conditions.

a. Sulfur-based plants

b. By-product gypsum-based plants

c. Pyrites based plants.

a. Sulfur-based plants : Table 56 contains the cost details for such a plant for the year 1970. This enables one to evaluate the cost for different raw material and utility prices and also for different interest rate, labor and supervision conditions. Table 57 is designed first by converting the 1970 investment value of Table 56 by using the Plant Cost Indices from Table 59 to 1973 value; second, substituting raw material, utility, labor and supervision prices prevailing in Turkey for 1973. The results indicate that a sulfur-burning plant of capacity 1000 tpd costs 56 million TL. and produces acid at the cost of 502 TL per ton.

b. By-product gypsum-based plants: Table 58 shows the cost details for gypsum based plants, here the investment value is converted to 1973 value by means of indices from Table 59 and the current prices for raw material and utilities of Turkey are substituted. The results give 587 TL per ton of acid if the plant pays for the raw material as anhydrite or natural gypsum; 418 TL per ton of acid if the fertilizer plant uses its own by-product calcium sulfate.

c. For a pyrites-based plant, Samsun (Azot) Plant is taken as an example and investment figure converted to 1973 value by means of Turkish conjuncture from Table 61, gives 220 million TL approximately (Table 60).

In addition, Table 62 gives some information about the production costs for various processes.

TABLE 56 : BREAKDOWN OF PRODUCT COST FOR 350,000 tons per year (1000 STPD) Sulfur-Based Plant (47)

Investment cost for battery limits plant :	$ 2,300,000
Investment cost for offsites:	300,000
Total investment (1970):	$ 2,600,000

Raw Material	Quantity	Unit cost	Annual cost	Product unit cost $/ST 100 % H_2SO_4
Sulfur	116,700 t.	36 $/ton	4,200,000	12.0
Utilities				0.58
Power(battery limits)	14,000 MWH	1 ¢/KWH	140,000	
Power(offsites)	3,000 MWH		30,000	
Boiler feed	500,000 t.	5 ¢/ton	25,000	
Process water	70,000 t.	2 ¢/ton	1,400	
Cooling water	700,000 t.	1 ¢/ton	7,000	
Steam(credit)	450,000	1 ¢/ton	450,000	(1.3)
Operating expenses				0.42
Labor	1 man/shift		32,000	
Supervision	parttime		10,000	
Maintenance	4 % investment		104,000	
Overheads				1.34
Payroll overhead	15% of (labor+supervision)		6,300	

TABLE 56: Cont'd

Raw Material	Quantity	Unit Cost	Annual cost	Product unit cost \$/ST 100 %H_2SO_4
General overhead	50% operating exp.		73,000	
Capital charges	15% investment		390,000	
Total manufacturing cost				13.04

The data herein permits an operator to evaluate the relative cost of acid produced from different sources available by using his own figures for raw material and utility costs and his own method of handling capital costs and returns. The result will not be an accurate estimate for cost of building a plant, but if it does not point to an overall advantage of one process or the other, it will be doubtfull if such advantage exists.

Table 56 indicates two points:

1. Except for very small plants which are no longer of interest in industrialized countries, the cost of the raw material is an overhelming proportion of the total production cost.

2. Economics obtainable from larger plants,

above about 1000 T/D are very small. Because, as the capacities of the plants are increased, the designers increased the flow areas and large vessels and towers have been used which reduced the cost advantages normally associated with the size.

In calculating the costs it is assumed that, essentially all steam is exported and all drives are electrical.

TABLE 57 : BREAKDOWN OF PRODUCT COST FOR 350,000 TPY SULFUR-BASED PLANT UNDER TURKEY'S CONDITIONS (3,50,55)

Investment cost for battery limits plant:

$$\$\ 2,300,000 \times \frac{148.6}{125.7} \times 14 = 38,100,000 \text{ TL}$$

Investment cost for offsites :

$$\$\ 300,000 \times \frac{148.6}{125.7} \times 14 = 4,970,000 \text{ TL}$$

Total investment : 43,070,000 TL

It is denoted in UNIDO Publications that the same type of investments cost 30 % more in developing countries than the industrialized ones; then:

Total investment : 56,000,000 TL.

	Quantity	Unit cost	Annual cost (TL)	Product unit cost per 100%H_2SO_4 (TL/ton)
Raw Material				
Sulfur(import)	116,700 tons	1850TL/ton	215,800,000	617
Utilities			6,375,000	18.20
Power(battery limits)	14,000 mwh	0.35TL/kwh	4,900,000	
Power(offsites)	3,000 mwh	0.35TL/kwh	1,050,000	
Boiler feed w.	500,000 tons	0.50TL/ton	250,000	
Process w.	70,000 tons	0.50TL/ton	35,000	
Cooling w.	700,000 tons	0.20TL/ton	140,000	

TABLE 57: Cont'd

	Quantity	Unit cost	Annual cost (TL)	Product unit cost per 100% H_2SO_4 (TL/ton)
Steam (credit)	450,000tons	130TL/ton	58,500,000	(167)
Operating expenses			2,387,600	6.82
Labor	1 man/shift	80TL/man/shift	87,600	
Supervision	part time	5000TL/month	60,000	
Maintenance	4 % of inv.		2,240,000	
Overheads			9,465,950	27.05
Payroll overhead	15% of(labor+ supervision)		22,150	
General overhead	50% of operating expenses		1,193,800	
Capital charges	15% of investment		8,250,000	
Total Manufacturing Cost				502.07

TABLE 58 : PRODUCTION COST FOR 1000 TPD CEMENT/ SULFURIC ACID PLANT IN TURKEY (3,50,117,139)

Investment (1968 prices) : $ 13,800,000

for Turkey, 1973 prices : 13,800,000x$\frac{148.6}{113.7}$x14x1.30=

328,000,000 TL

	Quantity	Unit Cost	Anuual cost, TL	Product unit cost per 100% H_2SO_4 TL/ton
Raw Material			116,600,000	353.3
by-product $CaSO_4$	694,000	-	-	(522.o)
(or)natural $CaSO_4$	694,000	80	55,520,000	
coke $CaSO_4$	33,000	700 TL/ton	23,100,000	
sand	550,000	70 TL/ton	38,500,000	
ash	550,000	100 TL/ton	55,000,000	
Utilities			86,168,500	261.0
electricity	4,950,000 kwh	0.35TL/kwh	1,732,000	
process w	33,000 ton	0.50TL/ton	16,500	
cooling w	23,100,000 ton	0.20TL/ton	4,620,000	
fuel(fuel oil)	57,000 ton	1400TL/ton	79,800,000	
Operating expenses			14,395,200	43.7
labor	2 men/shift	80TL/man/shift	175,200	
Supervision	1 man	750 TL/month	90,000	
Maintenance	4%of investment		14,130,000	
Overheads			21,395,200	64,8
Depreciation and interest	20%of investment		7,000,000	

TABLE 58: Cont'd

	Quantity	Unit cost	Annual cost, ₺	Product unit cost per 100 % H_2SO_4 ₺/ton
General and payroll overheads	(100%, operating ex)		14,395,200	
subtotal			238,558,900	
Less credit for clinker	330,000 ton	305 ₺/ton	100,700,000	(305)
Total manufacturing cost				417.8((586.5)

Plant for the dehydration of by-product gypsum may be 8-10 % more expensive than plant for the dehydration of natural gypsum which requires grinding before dehydration.

Therefore, the only significant addition to the operating cost of a kiln-acid plant when anhydrite is replaced with by-product gypsum, apart from those costs expressed as a percentage of the total fixed capital, is the cost of dehydrating the gypsum. The fuel requirement will depend on the free water content of the by-product gypsum and the thermal efficiency of the dehydrating equipment. This additional heat requirement is around 1500 tcal per ton of sulfuric acid.

As a **first** approximation, the plant cost of dehydrated gypsum less maintenance, is unlikely to differ appreciably from the cost of anhydrite if this is won where the acid is made.

TABLE 59: COST INDICES FOR USA (19,56)

Years	Marshall-Stevens indices for erected machinery and equipment Process industries; 1926=100	Engineering-News Record, construction indices; 1913=100	Plant Cost indices in chemical industries 1957-1959=100
1950	167	510	73.9
51	178	543	80.4
52	179	569	81.3
53	181	600	84.7
54	184	628	86.1
55	189	660	88.3
56	206	690	93.9
57	224	724	98.5
58	228	759	99.7
59	232	797	101.8
1960	237	824	102.0
61	236	847	101.5
62	237	872	102.0
63	238	901	102.3
64	241	936	103.2
65	244	971	104.0
66	252	1021	107.2
67	263	1070	109.7
68	273	1154	113.7
69	285	1271	119.0
1970	303	1380	125.7
71	321	1571	132.3
72	332	1752	137.2
73		1897	148.6
74			
75			
76			

TABLE 60: SAMSUN-AZOT SULFURIC ACID PLANT, INVESTMENT COST DETAILS OF THE PROJECT WITH 1967 PRICES (4)

Capacity : 215,000 tpy

	1000TL	%of total fixed investment
1. Project preparation	200	
2. Patent, know-how, etc.	3,200	
3. Land	100	
4. Site preparation	200	8.7
5. Construction works	8,300	
6. Transportation investments	100	
7. Mainfactory machinery and equipment	45,100	70.2
8. Auxiliary units machinery and equipment	9,000	
9. Transportation of machinery and equipment	2,400	
10. Imports expenses	-	
11. Montage expenses	13,000	
12. General expenses	3,600	21.1
13. Vehicles	600	
14. Commissioning	700	
15. Contingencies	6,500	
16. Interests (8 %)	6,100	
Fixed Investment Costs	99,000	
Working Capital	10,000	
Total Project Cost	109,000	

Fixed investment with 1973 prices:

$$I_1 = 99{,}000{,}000 \left[\frac{269.0}{122.3}(0.30) + \frac{274.4}{123.4}(0.70) \right]$$

$$I_1 = 220{,}000{,}000 \text{ TL}$$

TABLE 61 : INDUSTRIAL RAW MATERIALS AND AUXILIARY MATERIALS COST INDICES IN TURKEY (119)

	(1963=100)	General Index
1963	100.0	100.0
1964	102.7	101.2
1965	107.8	109.4
1966	112.2	114.7
1967	122.3	123.4
1968	128.8	127.3
1969	136.5	136.5
1970	153.6	145.7
1971	182.1	168.9
1972	222.4	199.3
1973	269.0	274.4

TABLE 62 : SULFURIC ACID PRODUCTION COSTS BY PROCESSES (1970)(133)

Process	Products	Conversion rate,%	Estimated Production Cost($) Dolars per short ton of acid (as100% acid)				
			50tpd	250tpd	340tpd	750tpt	1,500tpd
3-Stage contact, sulfur burning	<99 % acid	95	17.85	11.17	-	9.84	-
3-Stage contact, sulfur burning	acid+oleum	95	-	11.26	-	-	-
4-Stage contact, sulfur burning	<99 % acid	96	22.30	13.43	-	11.25	10.38
4-Stage contact, sulfur burning	acid + oleum	96	-	13.74	-	-	-
4-Stage contact, sulfur burning	<99 % acid	97.5	22.18	13.28	-	11.08	10.23
3-Stage contact, smelter gas	<99 % acid	95.8	16.79	5.20	-	2.95	-
4-Stage contact, smelter gas	<99 % acid	96.8	-	8.80	-	5.01	3.74
4-Stage contact, smelter gas	acid+oleum	96.8	-	9.12	-	-	-
4-Stage contact, smelter gas	<99 % acid	98.2	-	-	7.46	-	-

7.3. Some Important Factors Related to Cost and Nature of Production Methods (47) :

7.3.1. Contact Plants in General :

All contact plants can be conveniently divided into three sections:

a. Acid making-conversion and absorption
b. Gas purification
c. Gas production

a. Acid making :

Section 1 is essentially common to all plants. It includes the main blower, converter, drying and absorption towers and their associated heat exchange and heat removal equipment, Although there will be some differences in the latter depending on the gas source, these changes have little effect on the overall cost of the section. Overall cost of the section may be regarded, with sufficient accuracy, as a function of plant capacity and the available concentration of sulfurdioxide only. (Figure 11). For plants using x % sulfurdioxide, the cost used should be that of a plant of capacity 8/x times the actual plant capacity.

b. Gas purification:

This section is completely absent from normal sulfur burning plants where the gas produced is clean.

It includes equipment for removal of dust and sulfurtrioxide mist and in most cases includes only a wet scrubber and mist precipitator and associated equipment. The cost of the section depends mainly on the gas volume being treated. (Figure 12).

Another factor bearing on the cost of this section is the formation and disposal of weak acid. In almost all cases, the sulfurdioxide bearing gas will contain some sulfur trioxide which will form acid on cooling or contact with water. If this acid can be disposed of to a sewer, the cost of the plant will be a minimum. But, as this requires the use of large quantities of once through water as well as the disposal of weak acid amounting to perhaps 3 % of the product, the number of sites where this is acceptable for plants of substantial capacity is reducing. Another reason for increasing the cost of this section may be the necessity of recovering dust from the incoming gas.

Figure 13 plots the temperature to which the gas must be cooled for the production of 98 and 93 % acid at varying gas concentrations on the assumption that only dry air is added later.

c. Gas Production :

Real differences between acid plants occur in this section and these are then reflected to the other sections(Figure 14). It is convenient to consider two broad classifications:

c.1 Gas Production primarily for acid making:

This includes gas production from sulfur, hydrogen sulfide, pyrites and similar sulfur bearing ores and from acid sludge.

c.1.1 Sulfur and hydrogen sulfide burning :

Although in the former case gas produced goes directly to the acid making plant and to a purification plant in the latter, the equipment for the two plants are similar but differ only in size because of the higher heating value of hydrogen sulfide, and the section includes only the furnace, waste heat boiler and necessary auxiliaries.

c.1.2 Recovered acid plants:

Although a variety of processes have been used in the past to recover acid from refinery sludges and other waste acid, the trend for sometime has been to blend sludges so they can be burned in a furnace to produce a mixture of sulfurdioxide and carbondioxide with a minimum of excess air. This gas is treated in a normal purification and acid making plant. The equipment used is much the same for sulfur and hydrogen sulfide but because of the problems of burning these sludges, the furnace is usually larger and the burners more complex. The cost is, therefore, greater. These waste acid sludges vary so much in composition and properties that any cost information must be treated with reserve.

c.1.3 Pyrites :

Traditionally, equipment commonly used in the metallurgical industries has been adopted for the roasting of pyrites, but most recent plants have used fluid bed roasters. The size of the roaster will depend considerably on the size of the raw material and may be very large when the pyrites is a by-product from the floatation units and is therefore, finely ground.

c.2 Sulfur dioxide as a by-product of another operation :

This includes lead and copper smelter gases and similar operations where the gas production plant is not part of the acid plant. In this case, only capital charges which may be properly debited to the acid plant are the cost of connection.

c.2.1 Partial conversion to acid : here cyclic smelter operations are the sources of the gas, a facility for venting gas allows the selection of a plant capacity to meet average rather than peak gas production even where the demand for acid is high and this can result in considerable capital savings.

c.2.2 Substantially complete conversion to acid:

In cases where either because of acid demands or local conditions all the sulfurdioxide normally produced must be converted to acid but where it is possible in emergencies, to vent the smelter gas to the atmosphere, acid plant will be chosen to meet the peak gas production conditions and this can lead to a very expensive plant.

c.2.3 Complete Conversion to acid :

Where the plant is located in a populous district, it may be essential to accept into the acid plant all the sulfurdioxide the smelter produces. The smelter operator usually takes the position that his operation must not be inhibited by anything that happens on the acid plant and this may require the installation of more spare equipment than would otherwise be used.

In Table 63 operating utility requirements are listed which are based on the use of electric power for the main blower drive.

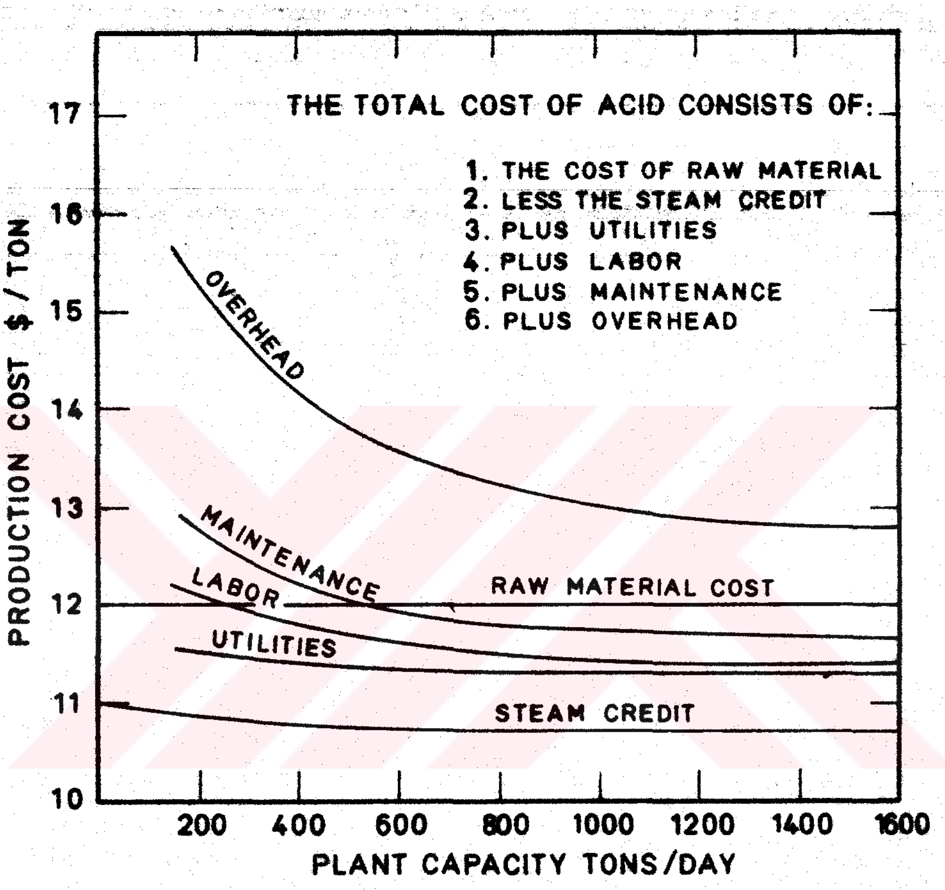

FIGURE 10 : Cost of acid at different production rates. (47)

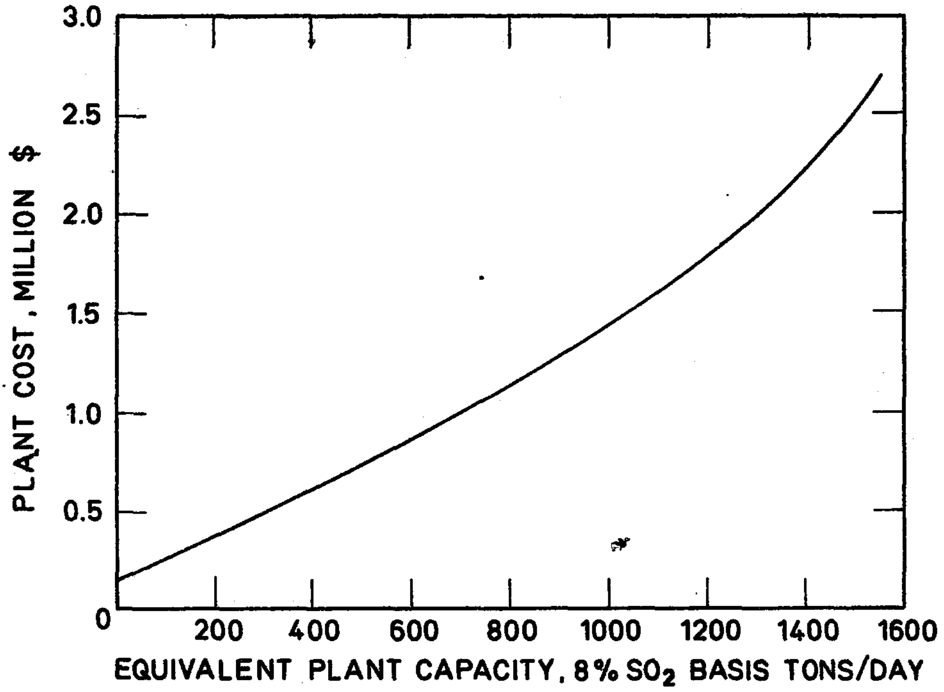

FIGURE 11: Cost of acid making section. (47)

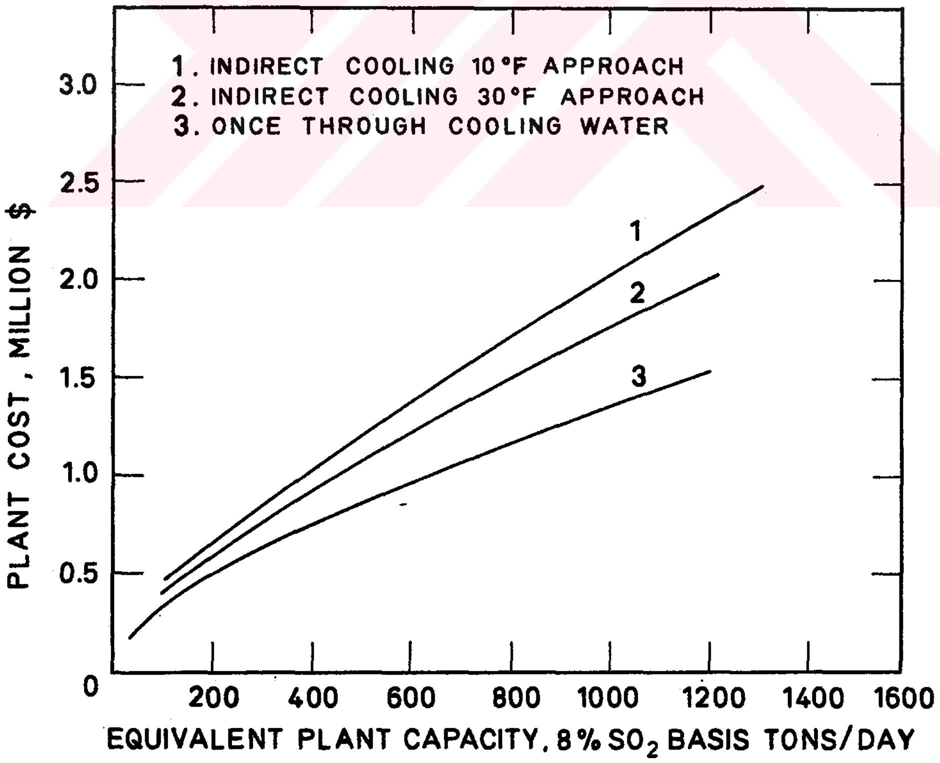

FIGURE 12: Cost of gas purification section. (47)

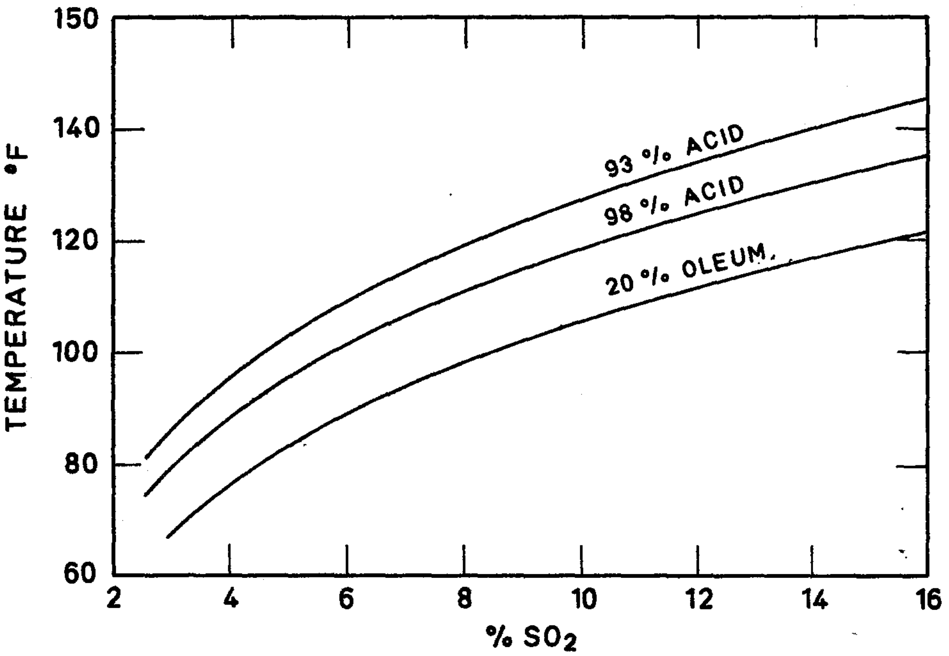

FIGURE 13: Gas temperature for various acid concentrations. (47)

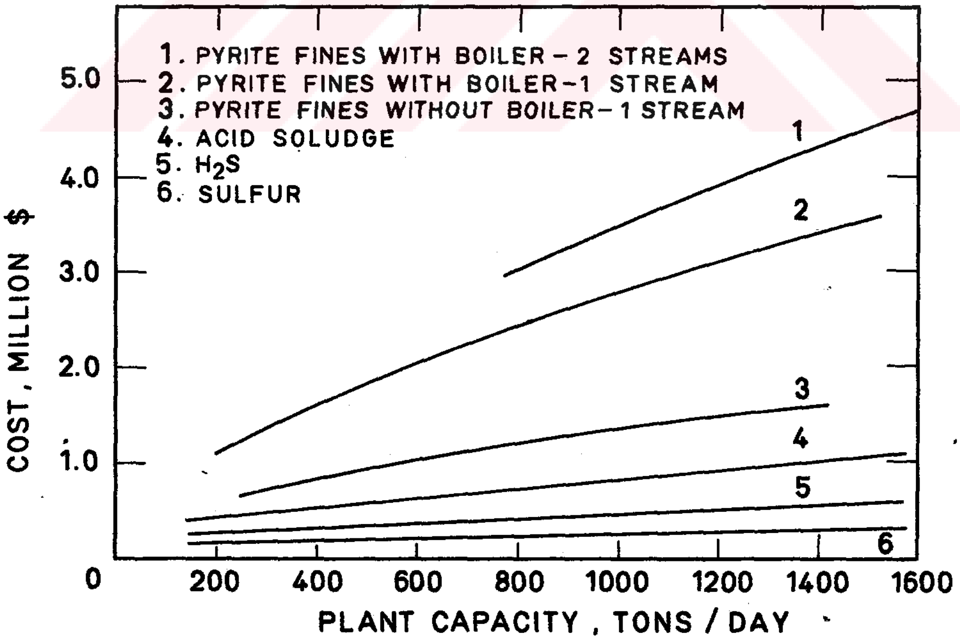

FIGURE 14: Cost of gas production section (47).

TABLE 63 : OPERATING REQUIREMENTS OF CONTACT PLANTS (47)

1.	Acid Making	per ton 100 % acid	
	Power	kwh	40-50
	Cooling water 85°F	tons	30
	Process water	tons	0.2
2.	Purification		
	Power	kwh	7-10
	Cooling water (once thru)	tons	10-25
	or recirculated	tons	15-40

3.	Gas Production		Sulfur	H_2S	Sludge	Pyrites
	Power	kWh	0.5	0	3	40-50
	Cooling water	tons	0	0	0	0
	Boiler feed water	tons	1.4	1.9	10-20	0.7-1.5
	Process water	tons	0	0	0	0.7

7.3.2 Power Systems :

About 60 % of the total reaction heat of a sulfur using contact plant is recovered in steam in a modern unit.

Although it is not possible to lay down any firm criteria for deciding the best recovery system, the following guidelines may be useful:

a. Where energy recovered is valued only for the heat content, the steam should be generated at the lowest possible pressure consistent with using it all in a back pressure turbine to drive the blower. This will lead to the lowest cost heat recovery equipment; the heating value of the low pressure steam produced will be as high as in any other system. This condition will generally apply where phosphoric acid is the only product, but may also apply in titanium dioxide production and in the general chemical field.

b. Where high pressure superheated steam is required, steam production should be at matching conditions and the blower driven by a condensing, back pressure or extraction turbine depending on the magnitude of the low pressure steam demand, if any. This will generally be the condition in large fertilizer complexes.

c. Where there is no steam requirement but a use or market for power exists, then the most profitable plant will include a turbo-generator using all the available steam at the highest practicable pressure and temperature for power production in condensing turbines. This is combined with an electically driven main blower. In very large plants where the blower drive is of sufficient power to permit the use of a high efficiency turbine, this may be preferred to an electric drive. On plants up to about 1000 T/D, the lower cost of the motor driven blower combined with the improved efficiency of the larger power generation unit will be the best solution.

DISCUSSION AND CONCLUSION

In conclusion, it is expected to find suggestions for the capacity, location, production method, raw materials and cost of the plant to meet the deficit.

a. Capacity Selection:

For the determination of capacities, the export conditions and the internal demand deficit are both considered.

a.1 Export availability:

This requires the comparison of import prices (FOB) with the production costs of domestically produced sulfuric acids.

The proposed plants will most probably use sulfur as the raw material; in that case the production cost will be around 502 TL/ton (Table 61) based on the sulfur price of 1850 TL/ton. Whereas the average selling price of technical grade sulfuric acid from existing plants in Turkey is around 900 TL/ton.

The import prices for the technical sulfuric acid is around 38 $/ton (CIF) (532 TL/ton),(Table 17) for 1973. The total cost of the import acid to the buyer after the customs and duties becomes 780 TL/ton.

Under these conditions domestic production appear to be more economical and advantageous, but the difference is small and can be overcome if the sulfur price is increased to 1940 TL/ton.

Against the rapid increases in raw material costs, this small difference seems rather risky for deciding on the establistment of export-oriented plants which would require some additional investment related to transportation facilities.

a.2 Internal demand deficit:

In the evaluation of sulfuric acid deficit in Turkey (Chapter 3), various approaches have been studied, and approach 2 is found to be more reliable. This approach (Table 28) gives a deficit from 1981 on.

In the determination of capacity, the selection has to be done in the optimum range. As it is noted in Chapters 6 and 7 the most recently built and projected. plants are not less than 750 tpd capacity. If the plant assumes to use first-hand raw material (sulfur, pyrites, natural gypsum and/or anhydrite) the plant capacity can be selected as 1000 tpd. If it is planned to consume second-hand raw material (such as smelter gases, by-product gypsum) the capacity of the sulfuric acid plant is largely dependent on the operation of the copper smelter and the fertilizer plant.

To meet the deficit, it is seen that 3x330,000 tpy plants could be erected by 1982, two of them coming on stream in 1981, one in 1982. Assuming the project preparation – erection-commissioning period takes three years, the project preparation should start in 1977.

b) Raw Material Selection :

The cost of sulfuric acid plants (Chapter 7) indicate that the sulfur-based contact plants are more economical than pyrites or sulfidic ore-based and gypsum-based plants.

In Turkey's case, two possibilities arise in the selection of raw materials :

1. to get maximum benefit out of domestic sources namely,
    - natural gypsum, anhydrite or by-product gypsum
    - smelter gases
2. to import sulfur.

These possible sources can be given priority as such with the following measures:

1. expansion of sulfuric acid-ex smelter gases plants,
2. addition of sulfuric acid units to smelters, if not existing,

3. using the residual gypsum feedstocks which create a waste problem in fertilizer plants,

4. building up gypsum-based sulfuric acid plants,

5. if the above proposals are unrealistic to operate economically and do not meet the deficit, then building plants basing on import sulfur.

1. The first measure has already been considered; Murgul's sulfuric acid capacity is planned to expand to 100,000 tpy, it is included into the 1974-investment program for the preparation of the project.

Ergani and Samsun smelters have sulfuric acid units at the economic scale.

2. To achieve the second measure, government may put some obligatory and promotive conditions for metallurgical units to convert their effluent sulfur dioxide to sulfuric acid, decreasing the pollution as well.

3-4. The production of sulfuric acid from gypsum (natural or by-product) and anhydrite proposal need to be studied in detail. As seen from the raw material chapter, estimated reserves of gypsum amount to 1,360,000,000tons with known S-content of 230,000,000 tons (55,111,148). The annual amount of waste gypsum from phosphatic fertilizer plants,at nominal capacity, can be approximated as follows (3) :

Plants	Nominal Capacity tpy	By-Product Calcium Sulfate tpy
Samsun I (TSP)	220,000	387,000
Samsun II (DAP)	139,500	608,000
Yarımca (TSP)	200,000	352,000
İskenderun (TSP)	200,000	352,000
Mersin (DAP)	148,500	646,000
Total		2,345,000

A 330,000 tpy capacity, gypsum-based sulfuric acid plant consumes 694,000 tons of gypsum (88,117) or anhydrite (Table 60). Both natural gypsum reserves and by-product gypsum sources are able to supply raw material to three such plants.

5. Comparison of Table 59 with Table 60 indicates that with 1973 prices a gypsum-based plant requires 328,000,000 TL of investment whereas a sulfur-based plant of the same capacity requires 56,000,000 TL. Simply for comparison purposes, a sulfuric acid plant similar to Azot-Samsun Plant (215,000 tpy) costs 220,000,000 TL in 1973.

The production costs for gypsum-based plant vary between 418-587 TL/ton depending on the variety of raw material as gypsum, anhydrite, by-product gypsum or mixes; whereas the production cost of sulfuric acid in a sulfur-based plant is around 502 TL/ton.

Under the prevailing conditions in Turkey, it can be concluded that after careful investigations and design of gypsum based plants, importation of sulfur takes the second place in the choice of raw materials.

c) Production Method Selection :

As described in detail in Chapter 5, the DC/DA process is the most advanced modification of the contact process with increased efficiency of conversion, thereby decreasing the pollution.

d) Site Selection :

As generalized by many authors, availability of raw material, price of raw material and the end use of sulfuric acid, more than any other factor determines the location of the sulfuric acid plants.

In this analysis, the selection of raw material results for sulfur, which will be imported. Therefore, the unique factor determining the location of the plant is its end use. This means that the sulfuric acid plants will continue to be erected nearby phosphatic fertilizer plants sometime, until chemicals industries grow up to need a sulfuric acid plant at the optimum capacity.

The master plan of fertilizer sector (82) indicates the deficit in phosphatic fertilizers by regions as follows, for 1980 :

	deficit (tons of P_2O_5)
Aegean region	71,685
Mediterrenean region	43,510
Western Black Sea Region	15,295

Here, the most recent four new fertilizer projects(119) are not included :

Ege Gübre Sanayii (1977-80):	240,000 tpy (20-20-0)
	26,500 tpy (18-23-0)
	40,000 tpy (15-15-15)
Total	P_2O_5 : 60,000 tons
Çukurova (TEKFEN)(1981-84)	330,000 tpy (20-20-0)
Total	P_2O_5 : 66,000 tons
Marmara-Thrace (TEGESAN)(1975-78) :	150,000 tpy (20-20-0)
	120,000 tpy (15-15-0)
Total	P_2O_5 : 48,000 tons
Marmara (İŞKUR)(1976-79)	200,000 tpy TSP(0-48-0)
	100,000 tpy DAP(14-46-0)
	100,000 tpy (20-20-0)
Total	P_2O_5 : 142,000 tons

Total P_2O_5 in Marmara Region : 190,000 tons

This shows that in 1980, total demand for phosphatic fertilizers will be supplied, almost together with their sulfuric acid requirements.

On the other hand, from approach 2 and 3 combined in Chapter 3, it can be concluded that the prohibition to the importation of sulfuric acid is essential in order to make full use of existing plants.

The most reliable approach to deficit in production of sulfuric acid appears as the second approach which concludes with the establishment of three sulfuric acid plants successively by 1982.

Although the initial investment for a gypsum-based plant is high, the production cost is competitive with the other methods. It is a fact that phosphatic fertilizer plants are in trouble with the removal or piling up of this by-product in Turkey. Even some of them are investing further for this purpose. The utilization of this by-product in acid factories as the raw material will not only avoid removal problems, but also will make the availability of the raw material safe against the import-based sulfur alternative. Therefore, more attention might be paid on this suggestion.

The presence of by-product calcium sulfate indicates that one plant near Samsun and a second one near Mersin-İskenderun Regions can be supplied with the raw material in excess; it could be thought that such a plant will be dependent on the fertilizer plant's productions but since a 1000 tpd capacity acid plant requires 694,000 tpy by-product gypsum as raw material, Samsun region will supply 995,000 tpy and Mersin-İskenderun regions will supply 998,000 tpy and Yarımca Plant will produce 352,000 tpy in excess.

It is seen that, takinginto account the approach 3 of Chapter 3, the proposal of establishing an acid plant near Yarımca Fertilizer Plant is in good aggrement with this suggestion too.

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APPENDIX A

STRENGTHS OF SULFURIC ACID AND ITS DETERMINATION

The strength of the acid is determined by a hydrometer test for strengths up to 66°Be (93.19%) and the strengths of acid weaker than 93.19 % is always expressed in degrees Baumé. Between 93.19 and 100 % sulfuric acid, the strength is spoken of as percent sulfuric acid and the electrical conductivity is a reliable and convenient method. Between 8 and 56 % free sulfurtrioxide, the oleums may be tested with a hydrometer; below and above these figures by titration with a standard caustic solution.

Commercial strengths of sulfuric acid are:

Chamber acid	50°Bé	62.18 % acid
Chamber acid	55°Bé	69.65 % acid
Glover acid or tower acid	60°Bé	77.67 % acid
Oil of vitriol("O.V")	66.Bé	93.19 % acid
Monohydrate		100.00 % acid
Fuming acid,or 20%oleum		104.49 % acid
40 % oleum		109.00 % acid

The Baumé scale for liquids heavier than water is based on the following relation to specific gravity:

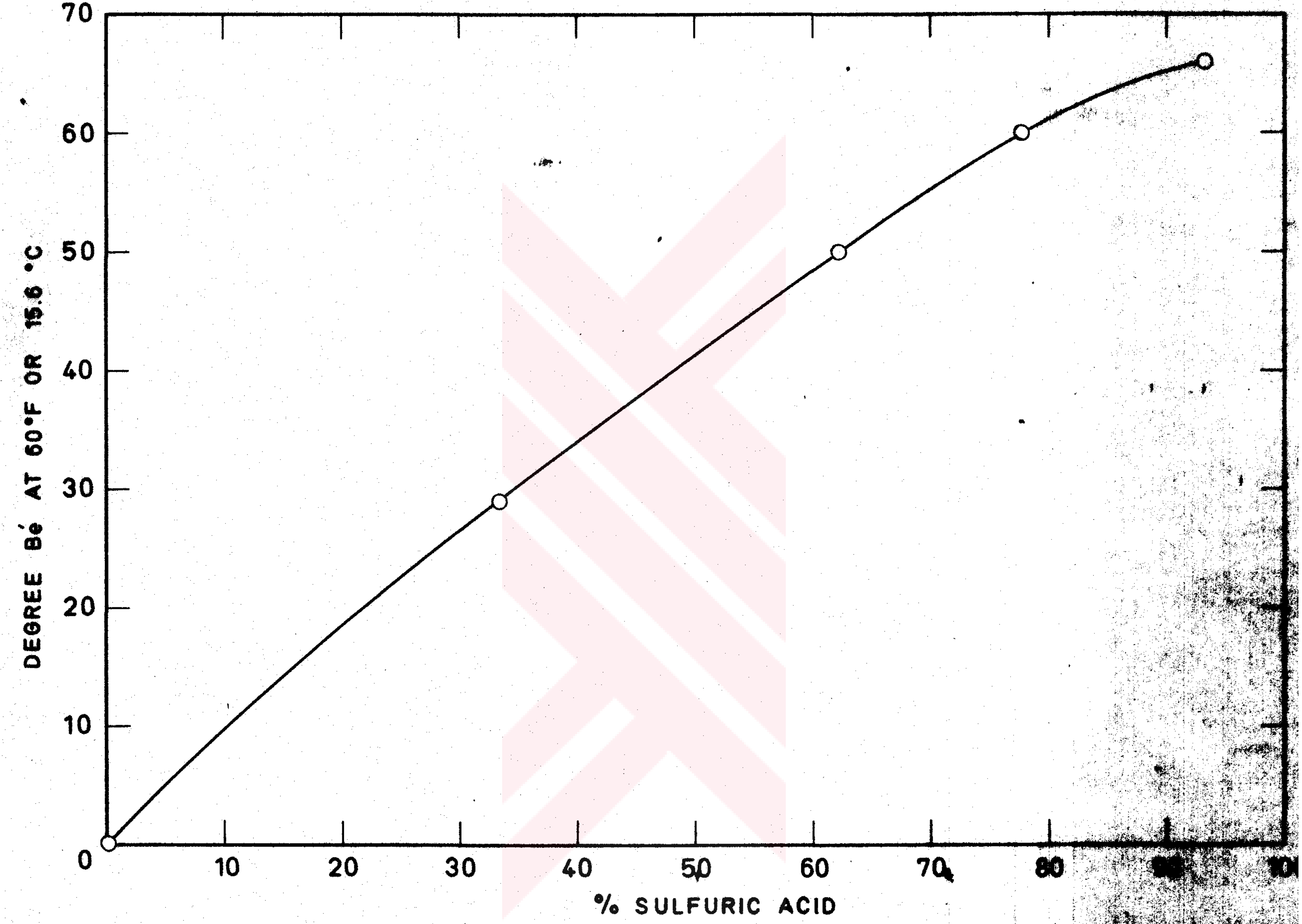
$$^{\circ}\text{Bé} = 145 - \left[\frac{145}{\text{sp.gravity } \frac{60^{\circ}}{60^{\circ}} \text{ F}} \right]$$

The figure 145 is known as the modulus of the hydrometer.

<u>Effect of temperature</u> : Because acid contracts as it cools and expands as it warms, it can be seen that the specific gravity will change with the temperature. A reference temperature of 60°F is used. Since it is impractical always to take a hydrometer reading at 60°F, correction factor must be applied to convert the reading to the base temperature. If the acid is warmer than 60°F, the correction is added to the observer reading, it is subtracted if the acid temperature is below 60°F.

Allowance for temperature:

Strength	per °F
10°Bé	0.029 °Bé
20°Bé	0.036 °Bé
30°Bé	0.035 °Bé
40°Bé	0.031 °Bé
50°Bé	0.028 °Bé
60°Bé	0.026 °Bé
63°Bé	0.026 °Bé
66°Bé	0.0235°Bé



APENDIX A : Concentration of Sulfuric Acid, °Bé vs % ([illegible])

APPENDIX B

TURKISH STANDARDS

There are 4 standards prepared by Turkish Standards Institutes all of them being optional:

1 - oleum (fuming sulfuric acid)

2 - pure sulfuric acid

3 - technical grade

4 - battery grade

1. OLEUM : TS 695 - prepared in January 1969.

Definition: Oleum is a light, colorless, non-transparent, rather viscous, very hydroscopic, very corrosive, strong and dangerous inorganic acid. It gives heat when mixed with water.

This standard covers only the oleum which is used in organic technology, especially in explosives manufacture, The pure and technical acids used in food and pharmaceuticals industries and accumulator production are not included in this standard.

Classification:

The oleum which is shipped to the market is classified into two groups according to the sulfur trioxide percentage:

Type 1 - Oleum 20

Type 2 - Oleum 45

Properties (Physical and Chemical) :

Properties	Type 1 Oleum 20	Type 2 Oleum 45
Appearance	a little opaque	a little opaque
Color	colorless	colorless
Free SO_3 min.	21 ± 1.0	45 ± 1.5
Residue of calcination max.%	0.02	0.02
Fe max %	0.004	0.004
Cl max %	0.02	0.02
As max %	0.01	0.01

Note: Percentages are on weight basis.

In transportation and continuous storage of type 1 and type 2 only glass and iron material must be used.

2. SULFURIC ACID PURE AND ANALYTICALLY PURE :
TS 693 - January 1969.

Definition : Pure sulfuric acid is a clear, colorless, rather viscous, hydroscopic, very corrosive and dangerous inorganic acid. It evolves heat when mixed with water. It kills the organic tissue. This standard does not include accumulator acid, technical grade acid and oleum. It only covers the acid used in chemical analyses and industrial branches which require concentrated acid.

Classification : The acid shipped to the market is classified into two groups according to the ingredients present:

Type 1 - Pure Sulfuric Acid

Type 2 - Analytically Pure Sulfuric Acid.

Physical and Chemical Properties:

Properties	Type 1 Pure acid.	Type 2 Analytically Pure acid
Appearance	clear	clear
Color	colorless	colorless
Specific gravity min. (15°/4°C)	1.84	1.84
% H_2SO_4 min.	96.0	96.0
Residue of calcination % max	0.003	0.001
Fe max %	0.002	0.0001
As max %	0.0002	0.000005
Cu max %	0.005	0.0001
Cl max %	0.001	0.0001
Pb max %	0.001	0.0003
Se max %	0.001	0.0002
SO_2 max %	0.003	0.0005
NH_3 max %	0.001	0.0003
NO_3 max %	0.001	0.0002

Reduced material total (max. usage of 0.01 N $KMnO_4$ for 100 ml. sample) ml	5	2.5

Note: Percentages are on weight basis.

3. SULFURIC ACID (TECHNICAL GRADE) : TS 692-January 1969.

Definition : Technical Sulfuric Acid is a reddish-brown (according to the iron and manganese content), a little opaque, rather viscous, hydroscopic, very corrosive and dangerous inorganic acid. It evolves heat when mixed with water, and kills the organic tissue.

This standard includes sulfuric acid used in superphosphate, amonium sulfate, other fertilizers, boric acid, copper sulfate, chromium salts productions, it is also used in other inorganic technologies, in metal pickling, and in technologies where SO_3 content is not limited. Accumulator acid, pure sulfuric acid and oleum are not included.

Classification : The acid shipped to the market divided into two groups according to the water and ingredients content :

Type 1 - 60 °Bé Sulfuric Acid

Type 2 - 66 °Bé Sulfuric Acid.

Physical and Chemical Properties:

Properties	Type 1 60°Bé acid	Type 2 66°Bé acid
Appearance	a little opaque	a little opaque
Color	colorless-red-brown	colorless-gray
(15°/4°C) min.	1.700(59.5°Bé)	1.800(65.0°Bé)
H_2SO_4 min %	77.17	90.05
Residue of calcination max %	0.15	0.20
Fe max %	0.035	0.04
As max %	0.04	0.04
Pb max %	0.05	0.06
NO_3 max %	0.01	0.01

Note : Percentages are on weight basis.

In transportation and continuous storage of type 1 (60°Bé) acid only lead or lead coated material; and for type 2 (66°Bé)acid iron material is used.

4. SULFURIC ACID BATERY GRADE : TS 694-January 1969.

Definition : Accumulator acid is a clear, colorless acid, rather viscous, hydroscopic, very corrosive (when concentrated) inorganic acid. It kills the organic tissue. when it is concentrated.

This standard covers the acid which is directly or in water solution used in accumulators. It does not include the technical sulfuric acid or pure sulfuric acid or oleum.

Classification : It is classified according to the acid contents.

- Type 1 - dilute accumulator acid
- Type 2 - concentrated accumulator acid.

Physical and Chemical Properties :

Properties		Type 1	Type 2
Appearance		clear	clear
Color		colorless	colorless
Specific gravity(15°/4°C)		1.230±0.010 (27.0±1.0Bé)	1.830±0.005
H_2SO_4	min %	31.10±1.20	92.0
Calcination Residue	max %	0.01	0.03
Fe	max %	0.0015	0.005
As	max %	0.0002	0.0006
Cu	max %	0.0015	0.005
Cl	max %	0.0007	0.002
Mn	max %	0.00003	0.0001
Sb	max %	0.0003	0.0001
Se	max %	0.0006	0.002
SO_2	max %	0.001	0.003
NH_3	max %	0.005	0.015
NO_3	max %	0.0005	0.0014
Reducing material (max usage of 0.01 N $KMnO_4$ for 100 ml sample)	ml	6.5	20

Note: Percentages are on weight basis.

In these standards, principles related to sampling from bottles, wagons and stock depots ; analyses, marketing and packing are stated.

Accumulator acid is shipped to the market either in small or large glass bottles.

APPENDIX C

MATERIALS OF CONSTRUCTION FOR SULFURIC ACID PLANTS: (87)

The metals now customarily used to handle cold sulfuric acid are: lead or stainless steel for strengths up to 95 %, steel or iron for strengths over 75 %.

For hot acid, lead is safe only up to 80 %, and steel and iron can be used only above 93 %, and then only in the absence of agitation which washes off the protective coating of sulfate. Therefore for hot acid between 80 % and 93 %, cast irons containing 14 % silicon (duriron, corrosiron, tantiron, etc.) are used, or, if greater tensile strength is required, high-nickel alloy such as "Hastelloy D". Ceramics and acidic brick are used for all strengths and temperatures.

<u>Tanks:</u> Generally, tanks should be designed to hold at least 50 percent more sulfuric acid than can be delievered by the delivery method normally used.

Sulfuric acid less than 54°Bé should be stored in phenolic-lined tanks or chemical lead-lined tanks. Above 60°Bé, mild steel is recommended as long as temperatures stay below 100°F. Strengths of sulfuric acid between 61°Bé and 66°Bé and between 99 percent and 101.5 percent should be stored in steel only when the temperature is kept below 75°F and moist air is excluded from the tank.

Certain grades of sulfuric acid such as electrolytic grade acid must be kept free from contamination with iron.

Welded construction is preferable for all sulfuric acid tanks. Generally, prefabricated tanks up to 27,500 gallons are available.

Steel sulfuric acid tanks may require washing every few years to clean the accumulated iron sulfate from the tank. Immediately after washing has been completed, the tank should be refilled with acid to prevent severe corrosion.

Sulfuric acid storage tanks are usually installed on a concrete pier with steel grillage so that the entire tank is visible for inspection and leak correction.

Pumps: Standard horizontal or vertical submerized centrifugal pumps are suitable for use with sulfuric acid. Iron pumps give satisfactory service but 20-series alloys (such as Worthite and Durimet 20) give superior service. High silicon cast iron (such as Duriron and Corrosiron) has excellent corrosion resistance and is frequently used where corrosion rates of many other materials are extremely high. However, this material is available only in castings and is mechanically and thermally brittle.

Gaskets: Ring gaskets for use with sulfuric acid are generally made from either 1/16-inch sheets of tetrafluoroethylene, chlorotrifluoroethylene, or compressed asbestos. The synthetic materials are particularly recommended for service with hot acid. Envelopes of synthetic materials are also frequently used.

Valves: Iron and steel valves can be used with sulfuric acid. However, iron sulfate forms radiply on these materias. This tends to interfere with performance. Therefore, valves made from alloys most resistant to corrosion are best suited for use with sulfuric acid.

Piping: All-welded schedule 80 black steel pipe with forged welding fittings and series 15 welding-neck or slip on weld flanges are generally used in sulfuric acid service. Cast iron or malleable iron cannot be used with oleum.

Acid lines should be kept full to minimize corrosion and excessive sulfonation. However, since it is occasionally necessary to empty acid lines for maintenance purposes, they should have sufficient pitch to permit complete draining. Sulfuric acid pipes should not be blown with air unless absolutely necessary, If air blowing is necessary, dry air must be used to minimize corrosion.

Cast iron pipe is generally preferred to steel for use with hot acid to the temperature limit for such materials. Since cast iron pipe is fragile, it must be handled with care and well supported when installed.

Since iron sulfate forms during sulfuric acid storage, care must be taken to avoid clogging pipe lines. Generally, pipe larger than one inch in diameter is necessary. Also, as the pipe diameter is enlarged, acid velocity is reduced and corrosion rates are substantially lower. For this reason, larger diameter pipe is recommended. In any case, acid velocity should never one foot per second in steel pipe two inches in diameter or less nor should it exceed two and one half feet per second in larger pipe.

Highly flammable hydrogen gas may be generated by the action of sulfuric acid on metal pipes. For this reason, the valve at each end of a line should be vented, preferably back to the storage tank, so that the hydrogen gas does not accumulate.

Rubber hose is attached by solutions of sulfuric acid more concentrated than 50°Bé. Tetrafluoroethylene and chlorotrifluoro-ethylene hose give satisfactory performance with all concentrations of sulfuric acid at temperatures upto 375°F.

Oleum: Oleum is handled like strong sulfuric acid. Recommendations for materials of construction for tanks and equipment given above can be applied to oleum with one exception. Cast iron, stainless steel type 316 and high silicon cast iron have very high corrosion rates with oleum and must not be used.

CORROSION OF MATERIALS BY SULFURIC ACID
(87)

Metals	dilute acid		strong acid	
	cold.	hot	cold	hot
Platinum	nil	nil	nil	very slight
High-silicon cast iron with(13-15% silicon)	nil	nil	nil	very slight
Lead	very slight	slight	slow $<$95%	slow $<$ 80%
Monel metal	very slight *	slowly att.	very slight*	attacked
Stainless steel 18% Cr,8% Ni	resistant *		$<$85% resistant *	
	attacked +	attacked *	attacked *	attacked
Stainless steel high Ni content	resistant	fairly resistant	resistant	fairly resistant
Iron or steel	attacked $<$ 65 %	attacked $<$ 93 % or $>$50°C	safe $>$75%	slow $>$ 93%

Non metals				
Silica	nil	nil	nil	nil
Sulfur	nil	nil	nil	slowly attacked
Rubber	resist $<$ 50%	resist $<$50% if $<$85°C	attacked $>$50%	attacked $>$50% or $>$ 85°C
Concrete, brick, masonry containing basic constituents	bad	bad	bad	bad
Paints, varnishes, enamels, and lacquers	some withstand	practically all attacked		

Note: The designation "nil" indicates absence of noticeably attacks, or a loss of weight of less than 1 mg per sq dm.

* If the acid contains dissolved air.

\+ Air - free acid.

APPENDIX D

STORING, WASHING, SHIPPING, UNLOADING AND SAFETY PROBLEMS IN SULFURIC ACID MANUFACTURE(142)

STORING SULFURIC ACID: Vertical or horizontal tanks are suitable for storing sulfuric acid. For all grades of acid furnished by the Tennessee Corporation, for instance, mild steel is the cheapest and best material of construction. If iron pickup must be avoided, the tank should be lined with a baked-on phenolic resin.

WASHING STORAGE TANKS: Storage tanks in sulfuric acid source will accumulate iron sulfate sludge. This sludge must be removed periodically to maintain the purity of the acid. The intervals between cleanings depend on such factors as the amount of acid handled, grade of acid, and humidity.

The reaction between weak acid and steel or cast iron forms hydrogen. Therefore, keep open flame or a welding arc away from the tank until it is thoroughly aired out, either by natural draft or forced ventilation.

SAFETY IN HANDLING: Sulfuric acid is the most widely used of all heavy chemicals. The huge tonnage consumed each year in varied industries proves that it can be handled safely if adequate precautions are observed. It is important to remember that sulfuric acid is a corrosive liquid. Even the weakest solutions are injurious to the skin and eyes, and higher strengths can cause severe burns. Protective clothing is essential in most operations. This includes rubber gloves, goggles or face shields, and in some cases rubber suits and boots.

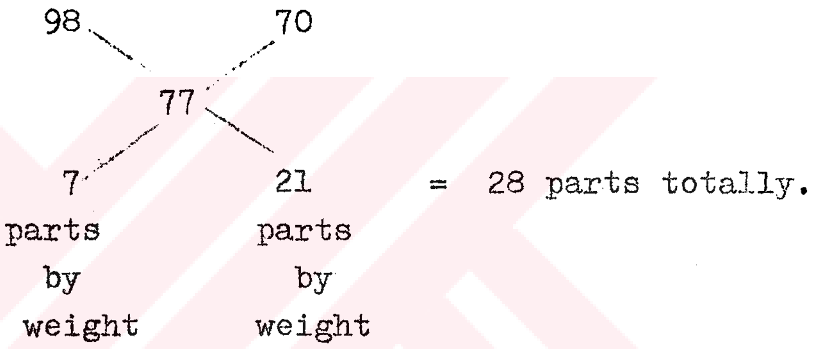
Since hydrogen is generated by the reaction of weak sulfuric acid on steel, it is recommended that smoking and open light be prohibited in storage tank areas, and that copper-beryllium (non-sparking) tools be used.

DILUTION OF SULFURIC ACID: Many times sulfuric acid is not used at the standard commercial concentration as delivered to the consumers. Two acids of different strengths may be mixed to form an acid of intermediate strength, or it may be desired to cut a strong acid with water to form a weaker one.

The rectangle **method**, used for many years, is the simplest means to solve the problem.

Using the rectangle method, the strengths of the two acids to be mixed are written on a horizontal line. The strength desired is placed below and between the two to be mixed. Now subtract the figures on the diagonals, the smaller from the larger, and place the result at the other end of the respective diagonal. The figures at the ends of the diagonals then indicate the parts by weight of the strength acid at the top ends of the vertical lines that must be mixed to get the desired strength.

Example: 77 % acid must be made by mixing 98 % acid 70 % acid.



When acid is diluted with water, one of the figures on the top horizontal line will be 0, as water has no acidity.

SHIPPING SULFURIC ACID: All tank cars used for shipping sulfuric acid in the Tennessee Corporation, have a nominal capacity of either 7,000 or 7,700 gallons. The net weight varies from 49-60 tons, depending on the strength of acid contained. Many are lined with a phenolic resin which presents iron pickup from corrosion during transit.

UNLOADING SULFURIC ACID: Sulfuric acid is always unloaded through a well pipe extenting to the bottom of the car or truck. A well or shallow depression in the bottom of the tank, permits the pipe to extend below the lowest part of the shell, thus allowing complete unloading of the acid. Both rail cars and trucks have bottom outlets for cleaning purposes, but their use for unloading is prohibited. Trucks or cars can be unloaded by air pressure or by a pump. Air pressure should not exceed 30 psi., and the pump should be made of a suitable material.

APPENDIX E

UNIT CONSUMPTION DATA FOR SULFURIC ACID USE IN DIFFERENT CHEMICAL AND PROCESSING INDUSTRIES (20,166)

Products	Units of acid(100%) per mist of product
- Ethylalcohol via ethylsulfate from ethylene	1.2 kg/lt
- Isopropyl alcohol	1.0
- Sec.butylalcohol	0.85
- Aluminium sulfate, for paper and pulp industry	0.90
- Ammonium sulfate	0.76
- Lead storage batteries,USA average	1.95 kg/battery
- Boric acid, ex sodium borates	0.44
- Boric acid, ex cholemanite	0.75
- Catalysts for cat-cracking in refineries	0.40-0.50
- Rayon, oven dry net	1.25-1.30
- Cellophane	1.00
- Cellulose acetate	0.05
- Sodium dichromate $2H_2O$	0.352
- Chromic acid	1.044
- Chloral + DDT (integrated plant)	1.60/t DDT

- chloral (only)	0.49
- DDT ex purchased chloral	1.23
- Nitration products+explosives	vary
- Normal superphosphate	1.786/ton P_2O_5
- Wet-process phosphoric acid	2.681/ton P_2O_5
- Hydrochloric acid,from salt	1.4
- Hydrofluoric acid ex fluorit (fluorspar)	1.33
- Iron and steel pickling,overall average	0.19 kg/ton steel
- bars	6.80 kg/ton bars
- wire	30.40 kg/ton wire
- Petroleum refining (alkylation)	14.5-16.3 kg/bbl or 0.1 kg/lt alkylate
- Phenol, via sulfonation of benzene	1.65
- Copper sulfate	1.60
- Nickel sulfate	0.39
- Zinc sulfate	0.36
- Dodecylbenzene sulfonate, sodium salt	
- acid input (as 20 % oleum)	0.8
- acid out,: in sodium salt in sod.sulfate and sulfuric acid	0.1
as spend acid(72-78%)	0.4
- net acid consumed	0.4
- Titanium dioxide,ex.Ilmenite,gross	1.50
net	1.35
- Uranium processing,average	20-25 t acid/ton U_3O_8
or	18-136 kg acid/ton ore.

APPENDIX F

INTERNATIONAL PATENTS RELATED TO SULFURIC ACID MANUFACTURE : (183)

The information taken from "Sulfuric Acid Manufacture and Effluent Control" serves a double purpose in that it supplies detailed technical information and can be used as a guide to the U.S. patent literature in this field. As the author says, the U.S. patent literature is the largest and most comprehensive collection of technical information in the world, the technical information obtained from a patent is extremely reliable and comprehensive. Many of these patents are being utilized commercially.

SULFUR DIOXIDE FROM SULFUR

Elemental sulfur is the most important raw material for sulfur dioxide. The mining of sulfur by Frasch process involves pumping hot water under pressure into subterranean sulfur-bearing deposits where upon the sulfur melts and is brought to the surface by an air lift.

MELTING SULFUR

If sulfur is solidified after Frasch mining and received in solid form at the sulfuric acid plant, the first step must be melting to get the sulfur in a form which can be atomized easily and burned to give sulfurdioxide.

Freeport Sulfur

A process developed by D.A. Lipps, J.D. Best, and P.A. Rubero; US. patent 3,355,259; November 28,1967, assigned to Freeport Sulfur Company relates to an improved method and apparatus for the melting of solid sulfur and the heating of the resulting liquid to temperatures above the melting point. The objects of the process are to provide a method for melting moist, solid sulfur and heating the liquid so produced without mechanical agitation, foaming, or scaling and corrosion.

ATOMIZING AND BURNING SULFUR

Allied Chemical and Dye

A process developed by H.F. Merriam and H.H. Hummence; U.S. Patent 2,726,933; December 13,1955 assigned to Allied Chemical and Dye Corporation involves combustion of elemental sulfur to produce high quality sulfur dioxide free or reasonably so of sulfur and oxygen. According to certain aspects of the process, sulfur dioxide produced is used under controlled conditions to oxidize gaseous sulfides to form recoverable elemental sulfur and the elemental sulfur employed in the main process.

A process developed by J.G. Melendy; U.S. Patent 2,539,519; January 30, 1951; assigned to Allied Chemical and Dye Corporation relates to the treatment of burner gases, such as produced from sulfur or sulfide ores and other materials used in the manufacture of sulfuric acid by the contact process, to reduce corrosion of the blowers and steel piping employed in contact sulfuric acid plants.

Badische Anilin- and Soda - Fabrik AG

A process developed by G. Schachenmeier and K. Starke, U.S. Patent 3, 149,916; September 22, 1964; assigned to Badische Anilin - and Soda Fabrik AG, Germany is a method for the combustion of sulfur with oxygen-containing gases. More especially, it relates to an improved process of burning sulfur in sulfur burners of unique design which produces SO_2 as a result of continuing explosions of sulfur-air mixture.

Chemical Construction

A process developed by L.N. Allen, Jr., U.S. Patent 2,622,007; December 16, 1952; assigned to Chemical Construction Corporation involves the manufacture of sulfur dioxide and is particularly directed to sulfur dioxide adapted for commercial utilization.

A device developed by K.M. Barclay and H.G. Bocckino; U.S. Patent 3,172,735; March 9, 1965; assigned to Chemical Construction Corporation is an improved apparatus for the spray burning of sulfur. An apparatus combination has been developed, which accomplishes a fine dispersion of sulfur droplets in air or other dispersion gas prior to complete combustion. As a result, complete and uniform sulfur combustion is attained using much smaller furnace volume.

Freeport Sulfur

A process developed by R.C. Hills; U.S. Patent 2,809,095; October 8, 1957; assigned to Freeport Sulfur Company relates to the production of sulfuric acid by the catalytic or contact method from so-called dark sulfur containing hydrogen.

Kimberly-Clark

A process developed by J.J. Shipman and J.W. de Vos; U.S. Patent 2,822,245; February 4, 1958; assigned to Kimberly-Clark Corporation relates to the manufacture of sulfurdioxide gas and more particularly to methods and apparatus for burning sulfur in relatively small, compact units.

Mathieson Chemical

A process developed by R.T. Braun; U.S.Patent

2,595,447; May 6, 1952; assigned to Mathieson Chemical Corporation relates to sulfur burners and more particularly to continuous sulfur vaporizer and burner systems. Among the several object of this process are the provision of sulfur vaporizer and burner systems for producing gas containing sulfurdioxide and vapor phase sulfur relatively free from impurities; the provision of sulfur vaporizer and burner systems which render possible closer control of effluent gas concentrations; and the provision of sulfur vaporizer and burner systems of the class described which effect a substantial increase in operating efficiency and unit production.

Standard Oil Development

A process developed by W.K. Lewis; U.S. Patent 2,608,467; August 26, 1952; assigned to Standard Oil Development Company is concerned with the production of sulfurdioxide and particularly the production of sulfur dioxide substantially free of sulfur trioxide, oxygen and sulfur.

Texas Gulf Sulfur

A device developed by I. Bencowitz; U.S.Patent 2,705,671; April 5, 1955; assigned to Texas Gulf Sulfur Company comprises certain structural arrangements for apparatus for burning sulfur, as in the manufacture of sulfuric acid, by first atomizing sulfur derived from a molten sulfur bath and then causing combustion to occur. It comtemplates particularly features which give rise to highly efficient combustion and which give to the apparatus a structural and operational simplicity making unnecessary any need for elaborate and costly equipment or delicate controls.

U.S.S.R.

A device developed by L.A. Bogdanov, E.I. Dorman, B.D. Katsnelson, M.P. Kavokin, J.V.Lastochkin, F.K. Mikhailov, L.M. Person, G.M. Saksonov, V.A. Slepnev, B.R. Bogdanov, and V.N. Khvastunov; U.S. Patent 3,519,397; July 7, 1970 is a cyclone type sulfur furnace employed in the production of sulfuric acid, comprising a cylindrical combustion chamber with nozzles for feeding primary air installed tangentially to the combustion chamber, the nozzles being partitioned lengthwise, thus allowing partial regulation of air supply to the chamber. The chamber also has tangential sprayers for sulfur-containing material and a diaphragm provided with radial channels through which secondary air is fed.

Walchandnagar Industries

A process developed by J.P. Mukherji; U.S. Patent

3,314,766; April 18, 1967; assigned to Walchandnagar Industries Limited, India relates to sulfur burners of the type in which the sulfur is vaporized from a pool of molten sulfur in the combustion chamber and the combustion of sulfur vapor takes place over the pool of molten sulfur, and in which a means is provided for varying the vaporization area of the molten sulfur, thereby controlling the rate of combustion of the sulfur without interfering with the air supply for that purpose.

SULFUR DIOXIDE FROM WASTE GASES

Although Frasch sulfur has long dominated the sulfur supply picture, production from various types of waste gases are growing and will ultimately outpace Frasch mining as a world source of sulfur. The figures for 1970 are roughly as follows:

	millions of long tons
Frasch sulfur	13
Sour gas recovery	9
Smelter recovery	12
	34

FLUE GASES

Air Preheater

A process developed by P.H.Karlsson; U.S.Patent 3,436,192; April 1, 1969; assigned to the Air Preheater

Company involves the continuous removal of sulfur dioxide from the exhaust gases generated by the combustion of fossil fuels in a boiler furnace. The system includes a sectionalized catalytic reactor to convert sulfurdioxide to sulfur trioxide, the reactor having flue gases passing through one section there of , the sections being independent of one another.

Chemical Construction

A process developed by E.Z. Finfer and H.P. Willett; U.S.Patent 3,533,748 ; October 13, 1970; assigned to Chemical Construction Corporation is one in which sulfur oxides are removed and recovered as elemental sulfur, from waste gas streams such as flue gas, by scrubbing the gas stream with an aqueous alkali solution. The solution absorbs the sulfur oxides, which react with alkali to form sulfite and sulfate in solution. The resulting solution is cooled to precipitate solid alkali metal sulfite and sulfate salts, which are separated from the solution and may be mixed with carbon. The salts or mixture is contacted at an elevated temperature with hot gases such as carbondioxide or a reducing gas such as a cracked hydrocarbon or natural gas, to liberate elemental sulfur vapor in a gas stream and convert the sulfite and sulfate to alkali, thereby regenerating the alkali which is recycled to the absorbing solution. The reducing gas stream is cooled to selectively condense the elemental sulfur product.

Hitachi

A process developed by Z. Tamura and Y.Hiskinuma; U.S. Patent 3,398,509; August 27, 1968, assigned to Hitachi , Ltd. Japan involves desulfurizing industrial waste gases by means of moving bed system using active carbon and having a low temperature adsorption zone, a high temperature adsorption zone, a desorption zone and a cooling zone arranged from the top to the bottom thereof, characterized in that a suitable amount of cooling water is injected directly into the cooling zone to directly cool the active carbon.

A process developed by Z.Tamma and Y.Hishinuma; U.S. Patent 3,486,852; December 30, 1969; assigned to Hitachi, Ltd., Japan involves the desulfurization of industrial waste gases by the use of active carbon which is regenerated repeatedly by rinsing it with water upon contamination and more specifically to improvements in the disposition of the water having been used in the rinsing and desorbing step in the process.

Ionics

A process developed by W.A. McRae, D.L.Brown and S.G. McGriff; U.S. Patent 3,475,122; October 28, 1969; assigned to Ionics, Incorporated is a cyclic process for the removal and recovery of sulfur dioxide from waste stack gases to lessen atmospheric pollution.

A process developed by E.J. Parsi; U.S. Patent 3,524,801; August 18, 1970; assigned to Ionics, Incorporated is a cyclic process for the removal of SO_2 from an SO_2-containing waste gas with subsequent recovery of at least some of the SO_2 in the form of sulfuric acid.

Lummus

A process developed by J.F. Thornton; U.S.Patent 3,475,121; October 28, 1969; assigned to the Lummus Company is a process for absorbing sulfurdioxide from a gas by introducing a finely divided alkaline earth metal oxide into the gas whereby the sulfurdioxide reacts therewith to produce the corresponding sulfite. The sulfite is separated from the gas, decomposed in a fluidized state to recover sulfurdioxide and the metal oxide and cooled for recycling to the absorption step.

Metallgesellschaft AG

A process developed by E. Pauling; U.S. Patent 3,318,662; May 9, 1967; assigned to Metallgesellschaft AG, Germany is a low temperature catalytic process for treating sulfur dioxide-containing gases in the presence of oxygen, water and a carbonaceous adsorbent or absorbent containing an effective catalytic amount of what was formerly thought to be a poisoning impurity.

A process developed by E.F. M. Pauling; U.S. Patent 3,294,487; December 27, 1966; assigned to Metallgesellschaft AG, Germany is a process for producing sulfuric acid where gaseous sulfurdioxide is catalytically reacted with oxygen in the presence of water at a temperature below about 120°C and where the gas is brought into contact with an adsorbent which is impregnated with a catalyst.

A process described by H.Müller-Wartenberg; U.S. Patent 3,475,133; October 28, 1969; assigned to Metallgesellschaft AG, Germany proposes an apparatus for the carrying out of a multistage method of purifying flue gases which contain sulfur compounds, and particularly the flue gases of oil or coal-fired boilers, the gases being subjected to a wet catalysis with preferred use of coal or carbon as catalyst in order to remove the sulfur-containing components and particularly sulfurdioxide, after the gases have been previously treated in coolers and scrubbers and had the dust removed from them possibly in mechanical or electrical dust precipitators, the cooler and/or scrubber, and if employed, the dust precipitator being arranged vertically one above the other with catalyst reaction beds in a tower-like common housing of preferably prefabricated plates forming a closed structural part which is developed as a gas shaft.

Mitsubishi Shipbuilding and Engineering

A process developed by M. Atsukawa, K.Matsumoto and H. Murokawa; U.S. Patent 3,226,192; December 28,1964; assigned to Mitsubishi Shipbuilding and Engineering Company, Limited, Japan is a process of treating a waste gas containing sulfuroxide with an absorbent, manganese oxide to render the waste gas harmless and more particularly a process of producing commercially valuable sulfuric acid and chlorine from such a waste gas with manganese oxide regenerated.

U.S. Secretary of the Interior

A process developed by D.Bienstock and J.H.Field; U.S. Patent 3,150,923; September 29, 1964; assigned to the U.S. Secretary of the Interior is an improved process for the removal of oxides of sulfur form waste gases.

PHOSPHATE PROCESS WASTE GASES

Hooker Chemical

A process developed by J.H.Hinkle,Jr.,E.J.Weaver and L.M. Smith; U.S. Patent 3,058,803, October 16,1962; assigned to Hooker Chemical Corporation pertains to the recovery of sulfur trioxide, and fluorine from waste gases effluent from chemical plants such as those for acidulation and/or calcination of phosphate minerals, e.g., phosphate rock.

VISCOSE RAYON PLANT WASTE GASES

Chemiebau Dr. A. Zieren

A process developed by H. Furkert; U.S. Patent 3,119,663; January 28, 1964; assigned to Fa. Chemiebau Dr. A. Zieren GmbH, Germany Relates to the recovery of hydrogen sulfide, carbondisulfide, carbonoxysulfide and similar sulfur compounds from moist waste gas, which sulfur compounds lend themselves to oxidation to SO_3 and in some instances also evolve H_2O and CO_2.

Reinluft GmbH

A process developed by F.Johnswich, U.S.Patent 3,284,158; November 8, 1966; assigned to Reinluft GmbH, Germany relates to the removal of compounds containing sulfur from industrial gases, especially the exhaust and waste gases of industrial processes, and more particularly, to the removal of reducing-sulfur compounds alone or concurrently with the removal of oxidizing-sulfur compounds from gas streams.

SULFUR DIOXIDE FROM HYDROGEN SULFIDE

ALLIED CHEMICAL

A process developed by H.F. Merriam and U.S. Lauber ; U.S. Patent 2, 629,651, February 24, 1953; assigned to Allied Chemical and Dye Corporation relates to the manufacture of sulfuric acid from H_2S-contaning gases.

METALLGESELLSCHAFT AG

A process developed by G. Rowedder; U.S.Patent 3,008,804; November 14, 1961, assigned to Metallgesellshaft AG, Germany involves the production of concentrated sulfuric acid and/or oleum from H_2S containing gases by the wet catalysis process.

SULFUR DIOXIDE FROM SULFIDE ORES

Sulfurdioxide is available as a by-product of the smelting of various sulfide ores. It not only offers an attractive economic incentive in the way of by-product recovery but may offer a means of eliminating atmospheric pollution as well.

COPPER ORES

Copper Range

A process developed by R.T. McKie; U.S. Patent 3,514,281; May 26, 1970; assigned to Copper Range Company is one whereby during extraction of copper from sulfide ore, smelter reverboratory smoke, which ordinarily is discarded as waste, is treated by a high efficiency multi-stage wet dust scrubber operating with an alkaline solution of lime, in order to produce, as a useful by-product, a sulfide matting agent and sulfuric acid or sulfuric acid only.

IRON SULFIDE ORES

Allied Chemical

A process developed by J.W. Swaine and J.C. Sloan, Jr.;U.S.Patent 2,785,050; March 12, 1957; assigned to Allied Chemical and Dye Corporation relates to the treatment of sulfide ore and more particularly, refers to a process for converting metal sulfides into sulfur dioxide gas and metal oxides.

A process developed by M.J. Brooks and J.W. Swaine; U.S. Patent 2,850,371; September 2, 1958; assigned to Allied Chemical Corporation involves an improved method for converting finely divided sulfide ore into sulfur dioxide and concomitantly effect the agglomeration of the finely divided particles in a single zone fluid burner.

Badische Anilin- and Soda - Fabrik AG

A process developed by A. Johannsen, W. Danz, W. Pfannmueller and H. Wolf; U.S. Patent 2,858,191;

October 28, 1958; assigned to Badische Anilin - and Soda- Fabrik AG, Germany relates to the production of gases rich in sulfur dioxide suitable for working up into sulfuric acid.

A process developed by A. Johannsen, W. Danz, W. Pflannmueller and H. Wolf; U.S. Patent 2,889,202; June 2, 1959, assigned to Badische Anilin- and Soda-Fabrik AG, Germany relates to improvements in the production of gases containing sulfur dioxide by roasting sulfur-containing ores.

A process developed by W. Pfannmueller, G.Wittman and H. Wolf; U.S. Patent 2,889,203; June 2, 1959; assigned to Badische Anilin- and Soda Fabrik AG, Germany relates to a process for the production of gases containing sulfur dioxide from materials containing roastable sulfur in addition to at least one of the elements arsenic and antimony with the recovery of roasted residues practically free from arsenic and antimony by step wise roasting said materials in fluidized layers.

A process developed by A. Johannsen, W. Danz, W. Pfannmueller and H. Wolf; U.S. Patent 2,993,778; July 25, 1961; assigned to Badische Anilin-and Soda-Fabrik AG, Germany provides a unique improvement in the roasting of a sulfur mineral such as comminuted pyrites with the production of sulfur dioxide in a fluidized bed, which involves introducing oxygen-containing gas above the bed to roast incompletely roasted mineral fines or dust entrained in the roaster gas leaving the bed.

A process developed by G.Wittman, U.S. Patent 3,198,602; August 3, 1965; assigned to Badische Anilin- and Soda - Fabrik AG, Germany involves roasting sulfidic iron ore containing roastable sulfur besides lead and at least one of the elements arsenic and antimony, by which process there are obtained roasted residues which are practically free from lead, arsenic and antimony.

Chemical Construction

A process developed by B.G. Mandelik ; U.S.Patent 3,059,995; October 23, 1962; assigned to Chemical Construction Corporation relates to sulfide ore roasting in which a dust-laden off-gas is produced which contains, in addition to sulfur dioxide, significant quantities of sulfur trioxide.

Dorr Oliver

A process developed by E.J. Roberts, R.M.Foley and D.F. Wells; U.S. Patent 2,625,464; January 13,1953; assigned to the Dorr Company relates to the roasting of ores or concentrates which contain metal sulfides, in order to yield thereby gaseous sulfur dioxide free from objectionable sulfur trioxide and suitable for the manufacture of sulfuric acid. It is particularly adopted for the roasting of sulfidic metallurgical solids which also contain iron sulfides.

A process developed by E.J. Roberts; U.S.Patent 2,867,506; January 6, 1959; assigned to Dorr-Oliver Incorporated relates generally to the production of sulfurdioxide gas from sulfur bearing ores.

A process developed by W.W. Jukkola; U.S.Patent 3,047,365; July 31, 1962; assigned to Dorr-Oliver Incorporated relates to means for temperature control in the fluidized bed roasting of sulfide ores.

Institut de Recherches de la Siderurgie Francaise

A process developed by M. Boucraut; U.S.Patent 3,189,437; June 15, 1965; assigned to Institut de Recherches de La Siderurgie Francaise, France relates to improvements in roasting by fluidization, more particularly to magnetizing roasting.

International Nickel

A process developed by G.H.C., Norman; U.S.Patent 3,042,498; July 3, 1962; assigned to the International Nickel Company, Inc. provides an improved apparatus comprising a furnace for suspension roasting finely divided sulfide materials to obtain calcine of exceptionally low sulfide-sulfur content while maintaining high treatment rates per unit of hearth area.

Metallgesellschaft AG

A process developed by I. Schytil and H.Ley;U.S. patent 2,756,986; July 31, 1956; assigned to Metallgeselschaft AG, Germany relates to the roasting of sulfide ores while suspended in a fluidized bed or a gas stream.

Montecatini

A process developed by I. Vaccari, P.Salle, A. Morra and U. Colombo; U.S. Patent 3,160,496; December 8, 1964; assigned to Montecatini Società Generale per I'Industria Mineraria e Chimica, Italy relates to the treatment of iron pyrites.

SULFUR OXIDES AND SULFURIC ACID FROM SULFATES

ALUMINUM SULFATE

North American Coal

A process developed by J.C. Udd, U.S. Patent 3,265,464; August 9, 1966; assigned to the North Coal Corp. finds particular application in the processing of hydrated aluminum sulfate for the production of cell-grade alumina which is amenable in all respects for use in the conventional Hall process reduction to metallic aluminum, or in other processes where such material is requried.

AMMONIUM SULFATE

Chemiebau Dr. A. Zieren

A process developed by H. Furkert and R.Schèrtz; U.S. Patent 3, 275,407; September 27, 1966; assigned to Chemiebau Dr. A. Zieren GmbH, Germany relates to a method of recovery of ammonia and sulfur dioxide from ammonium sulfate, ammonium hydrogen sulfate and from aqueous acidic solutions contaning and ammonium hydrogen sulfate, sulfuric acid and optionally organic compounds.

A process developed by H. Furkert and H. Mühlenbein; U.S. Patent 3,292,996; December 20, 1966; assigned to Chemiebau Dr. A. Zieren GmbH, Germany relates to a method of recovery of sulfur oxides and ammonia, in general, and in particular to such method for separate recovery of sulfur oxides and ammonia from ammonium hydrogen sulfate or sulfuric acid solution of ammonium sulfate, such as these often obtained in large quantities in the chemical industry.

A process developed by H.Furkert and H.Röhl, U.S. Patent 3,359,069; December 19, 1967; assigned to Chemische Werke Huls AG and to Chemiebau Dr.A Zieren GmbH, Germany relates to the production of sulfur dioxide-containing gases from waste products containing ammonium salts of sulfur acids.

Houdry Process

A process developed by T.H.Milliken, Jr.; U.S. Patent 2,926,070, February 23, 1960; assigned to Houdry Process Corp. relates to the treatment of ammonium sulfate and ammonium hydrogen sulfate to recover therefrom ammonia and the oxides of sulfur.

Inventa AG

A process developed by W. Deiters, U.S.Patent 3,243,261; March 29, 1966; assigned to Inventa AG für Forschung und Patentverwertung, Switzerland relates to the recovery of ammonia and sulfur oxides from ammonium sulfate liquors.

Stamicarbon NV

A process developed by A.H. de Rooij and J. Elmendorp ; U.S. Patent 3,364,202; January 16,1968; assigned to Stamicarbon NV, Netherlands relates to the recovery of free sulfuric acid, starting from ammonium bisulfate or a concentrated solution of this salt.

CALCIUM SULFATE (GYPSUM)

Farbenfabriken Bayer

A process developed by H. Zirngibl, U.S.Patent

3,129,063; April 14, 1964; assigned to Farbenfabriken Bayer AG, Germany relates to the production of sulfur dioxide from one of several inorganic sulfates.

IRON SULFATE

British Titan Products

A process developed by K.R.Hansford, A.L. Roberts, A.W. Evans and W. Hughes; U.S. Patent 3,195,981; July 20, 1965; assigned to British Titan Products Company Limited, England is concerned with the production of sulfuric acid from hydrated iron sulfate.

Chempro

A process developed by J.A. Patterson, U.S.Patent 3,053,626; September 11, 1962; assigned to Chempro, Incorporated relates to the treatment of solutions of heavy metal sulfates for the production of sulfur dioxide in a useful concentration and an end product in the form of oxide of the heavy metal or a mixture of said oxide with reduced particles of the heavy metal.

R.M. Lewis

A process developed by R.M. Lewis; U.S. Patent 3,153,575; October 20, 1964 relates to the treatment of spent pickle liquor which results from the acid cleaning of ferrous metal products.

North American Coal

A process developed by E.L. Clark; U.S.Patent

3,086,846; April 23, 1963; assigned to the North American Coal Corp. is a metallurgical process in which there is a separation of ferrous sulfate and/or other sulfates, as well as the decomposition of the sulfates to produce SO_2 and sulfuric acid.

Puriron and Chemicals

A process developed by C.B. Francis; U.S.Patent 2,946,659; July 26, 1960; assigned to Puriron and Chemicals, Inc. relates to the production of sulfuric acid from ferrous sulfate, and consists in certain new and useful improvements in pre-existing methods for the purpose.

SODIUM SULFATE

Reynolds Metals

A process developed by M.L. Garing, F.E. Adkins, Jr. and G.E. Branigan; U.S. Patent 3,207,575; September 21, 1965; assigned to Reynolds Metals Company relates to a method for the concurrent production of sodium aluminum fluoride and sulfuric acid from a waste by-product of the processing of bauxite or other aluminous ores in the preparation of alumina by the Bayer or Bayer-sinter process.

SULFURIC ACID FROM SULFUR DIOXIDE AND HYDROGEN CHLORIDE

DU PONT

A process developed by J. Kamlet; U.S. Patent

3,152,866; October 13, 1964; assigned to E.I, du Pont de Nemours and Company is a cyclic process for the conversion of hydrogen chloride and sulfur dioxide to chlorine and sulfuric acid.

UGINE KUHLMANN

A process developed by R. Bauwens and J. Molliere; U.S. Patent 3,414,377; December 3, 1968; assigned to Ugine Kuhlmann, SA, France involves producing chlorine from hydrogen chloride, where in mixtures of hydrogen chloride, sulfur dioxide, and possibly sulfur trioxide and other oxygen-containing gases are treated in the presence of a catalyst, thus making it possible to produce chlorine and sulfuric acid in one and the same operation.

SULFURIC ACID BY THE CHAMBER PROCESS

DU PONT

A process developed by J.A. Jenemann and E.B. Hollis; U.S. Patent 2,344,616; March 21, 1944; assigned to E.I. du Pont de Nemours and Company relates to the manufacture of sulfuric acid in lead chamber systems and provides simple and efficient methods for increasing production in such systems without requiring material alteration in equipment.

P.KACHKAROFF AND P. GUARESCHI

A process developed by P.Kachkaroff and P.

Guareschi, U.S. Patent 2,678,872; May 18, 1954 relates to method for the production of sulfuric acid from sulfur dioxide, oxygen and water by means of highly concentrated sulfuric acid which contains nitrogen oxides, free or combined, so called nitrous sulfuric acid.

J. MORITZ

A process developed by J. Moritz; U.S. Patent 2,791,49[illegible]; May 7, 1957, provides a succession of utilization of phases of reaction in liquid medium, followed immediately afterwards by phases of reaction in gaseous medium, owing to the combination of lead chambers and more particularly chambers with low communicating passages with internal reaction towers.

H. PETERSEN

A process developed by H. Petersen; U.S.Patent 2,258,938; October 14, 1941; relates to improvements in the chamber process for sulfuric acid manufacture.

CONVERSION OF SULFURDIOXIDE TO SULFUR TRIOXIDE SPECIFIC PROCESSES

D.B. Burkhardt

A process developed by D.B.Burkhardt; U.S.Patent 3,362,786; January 9, 1968 relates to a multistage catalysis in the oxidation of sulfur dioxide to sulfur trioxide and to trioxide concentration in such a process.

Chemical Construction

A process developed by M.H. Maurer; U.S.Patent 3,147,074; September 1, 1964; assigned to Chemical Construction Corporation relates to the production of sulfuric acid. An improved process sequence involving preheating of process air has been devised, which permits the improved recovery of process heat and also reduces equipment size and cost.

Farbenfabriken Bayer

A process developed by W.Möller; U.S.Patent 3,259,459; July 5, 1966; assigned to Farbenfabriken Bayer AG Germany involves the production of SO_3 by catalyst method in several stages, with interposition of an intermediate absorption, the method comprising reacting the gas residue, which remains after the removal of the SO_3 generated in the forward part of the system, in another catalyst furnace part at temperatures which are considerably lower, for example 20° to 60°C or 40° to 60°C lower, than the initiation temperature resulting prior to the dissolving out of the SO_3.

A process developed by H. Guth, A. Heitman, W. Möller and H. Werth; U.S. Patent 3,142,536; July 28,1964; assigned to Farbenfabriken Bayer AG, Germany involves the production of sulfur trioxide from SO_2 obtained from pyrites.

Imperial Chemical Industries

A process developed by D. Davies; U.S. Patent 2,799,560; July 16, 1957; assigned to Imperial Chemical Industries Limited relates to the production of catalysts for the oxidation of sulfur dioxide to sulfur trioxide.

Another process developed by P. Davies; U.S.Patent 3,186,794; June 1, 1965; assigned to Imperial Chemical Indistries Limited, England relates to the oxidation of sulfur dioxide to sulfur trioxide, and particularly to the production of catalysts suitable for use in this reaction.

Montecatini Edition

A process developed by A. Junginger; U.S. Patent 3,307,921, March 7, 1967; assigned to Montecatini Edison SpA, Italy relates to apparatus for controlling chemical reactor temperatures by means of superheated steam, and more particularly for the control of exothermic reactions carried out in catalytic multilayer systems or multistage exothermic reactions producing hot streams of fluids at or intermediate a plurality of stages.

R.M. Parsons

A process developed by T.J. Browder, Jr.; U.S. Patent 3,525,587; August 25, 1970; assigned to the Ralph M. Parsons Company is a multiple stage process for the production of sulfuric acid by the catalytic oxidation of sulfur dioxide-containing gas and the multiple stage absorption of sulfur trioxide produced by such catalytic oxidation.

Pullman

A process developed by B.G. Mandelik; U.S.Patent 3,282,645; November 1, 1966; assigned to Pullman Incorporated relates to the conversion of sulfur trioxide and, more particularly, to a method for the catalytic oxidation of sulfur dioxide to sulfur trioxide. Still more particularly, it relates to a method for improving the conversion efficiency and heat economy in the conversion of sulfur dioxide to sulfur trioxide.

Saint-Gobain

A process developed by R. Krempff, U.S. Patent 3,275,406; September 27, 1966; assigned to Compagnie de Saint-Gobain, France relates to the manufacture of SO_3 by the catalytic oxidation of SO_2 on vanadium-potassium-silica catalysts using catalytic granules of varying porosity.

Strategic Materials

A process developed by M.J. Udy; U.S.Patent 3,005,687; October 24, 1961; assigned to Strategic Materials Corporation relates to an improved process for the production of sulfuric acid.

CONVERSION OF SULFUR TRIOXIDE TO SULFURIC ACID AND OLEUM

ALLIED CHEMICAL

A process developed by H.F. Merriam and T. Cummings; U.S.Patent 2,562,240; July 31, 1951; assigned to Allied Chemicals and Dye Corporation relates to improvements in processes for manufacture of oleum.

BADISCHE-ANILIN- AND SODA-FABRIK

A process developed by W. Klinger and H.Wolf; U.S.Patent 3,232,705; February 1, 1966; assigned to Badische Anilin- and Soda-Fabrik AG, Germany relates to a process for the production of sulfuric acid, especially to a process for the production of pure concentrated sulfuric acid which is free from sulfur dioxide.

CHEMICAL CONSTRUCTION

A process developed by L.N. Allen, Jr and T.P. Forbath; U.S.Patent 2,655,431; October 13, 1953; assigned Chemical Construction Corporation relates to a method and apparatus for the production of sulfuric acid and more particularly to a method of absorbing sulfur trioxide from gases containing this material by contact with sulfuric acid.

FARBENFABRIKEN BAYER

A process developed by A. Haltmeier; U.S.Patent 2,730,431; January 10, 1956; assigned to Farbenfabriken Bayer AG, Germany relates to a process for the manufacture of sulfuric acid, and more particularly to a process for the manufacture of sulfuric acid by reacting by sulfur trioxide with sulfuric acid at temperatures of at least 150°C and of at most of boiling point of the sulfuric acid.

SONNEBORN CHEMICAL AND REFINING

A process developed by A.J. Bevevino and H. Sonneborn 111; U.S.Patent 3,116,972; January 7,1964; assigned to Sonneborn Chemical and Refining Corporation relates to an improved method for intimately contacting a compound in liquid phase, such as water, with a gas, such as SO_3, making possible the absorption by the liquid of the gas.

INTEGRATED CONTACT PROCESS PLANTS

SPECIFIC INDUSTRIAL PROCESSES

Allied Chemical and Dye

A process developed by H.F. Merriam; U.S.Patent 2,471,072; May 24, 1949; assigned to Allied Chemical and Dye Corporation relates to the manufacture of sulfuric acid by the contact process.

A process developed by B.M. Carter; U.S.Patent 2,520,454; August 29, 1950; assigned to Allied Chemical and Dye Corporation relates to improvements in the manufacture of oleum and sulfuric acid.

Boliden AB

A process developed by J.E. Wiklund; U.S.Patent 3,532,471; October 6,1970; assigned to Boliden AB relates to production of sulfuric acid and particularly to a device for controlling the concentration of sulfuric acid in a sulfuric acid plant's drying circuit for drying the sulfur dioxide to be oxidized to sulfur trioxide in an oxidation apparatus for this purpose, usually operating according to the contact process,

Chemical Construction

A process developed by A.L. Rugh; U.S.Patent 3,172,725; March 9, 1965; assigned to Chemical Construction Corp. is a method whereby concentrated sulfuric acid may be economically produced from the sulfur dioxide contained in dilute gas streams, such as smelter stack gases containing from 1 to 7 % sulfur dioxide.

A process developed by J.B. Rinckhoff ; U.S. Patent 3,350,169; October 31, 1967; assigned to Chemical Construction Corporation is one in which sulfuric acid is produced by dividing a sulfur dioxide-containing process gas stream into two porsions.

A process described by M.H.Maurer;U.S. Patent 3,536,446; October 27, 1970; assigned to Chemical Construction Corp. is another process variation in which the initial hot process gas stream produced by sulfur combustion is divided into two portions.

A process developed by E.O. Ohsol; U.S. Patent 3,432,263; March 11, 1969; assigned to Chemical Construction Corp. is a high pressure sulfuric acid process in which process air for sulfur combustion to sulfur dioxide is initially compressed to provide a high pressure process gas which flows through the catalytic system and sulfur trioxide absorption at high pressure, with subsequent expansion of the residual gas through a power recovery turbine.

Another high pressure sulfuric acid contact process variation is described by G R. James; U.S. Patent 3,455,652; July 15, 1969; assigned to Chemical Construction Corporation.

A process developed by M.H. Maurer and C.S. Benefield; U.S. Patent 3,475,120; October 28, 1969; assigned to Chemical Construction Corp. is one in which concentrated sulfuric acid is employed to scrub a gaseous sulfur dioxide-containing feed stream prior to catalytic sulfur trioxide formation in a sulfuric acid process, in order to remove water vapor from the feed stream.

A process developed by J.B. Rinckhoff; U.S. Patent 3,519,388; July 7, 1970; assigned to Chemical Construction Corp. is one in which a hot sulfur dioxide-containing gas stream, typically derived from a pyrites ore smelter or copper converter at a temperature above 100°C and containing less than about 8 % by volume of sulfur dioxide together with excess free oxygen and water vapor in an amount not more than that required for product acid, is employed as a sulfur source for the production of concentrated sulfuric acid.

Chemiebau Dr. A. Zieren

A process developed by H. Furkert, F. Mahler, H. Peters, and A. Stauffer, U.S.Patent 3,443,896; May 13, 1969; assigned to Firma Cheibau Dr. A. Zieren GmbH, Germany is one in which sulfuric acid is produced from sulfur dioxide containing gases utilizing a multistage catalytic sulfur dioxide oxidation and two stage sulfur trioxide absorption.

Du Pont

A process developed by I.R. McHaffie and H.R.L. Streight; U.S. Patent 2,415,142; February 4, 1947; assigned to E.I. du Pont de Nemours and Company relates to the manufacture of oleum and high strength sulfuric acid by the contact process and is particularly directed to the utilization of dry waste gases issuing from the system in reducing the moisture content of wet gases entering the system.

A process developed by R.R. Detweiler; U.S. Patent 3,454,360; July 8, 1969; assigned to E.I. du Pont de Nemours and Company is a method for making sulfuric acid comprising converting sulfur dioxide to sulfur trioxide, adiabatically transferring the sulfur trioxide to an absorber where it is contacted with water to make sulfuric acid and recovering the sulfuric acid.

Farbenfabriken Bayer AG

A process developed by A. Haltmeier ; U.S.Patent 2,879,135; March 24, 1959; assigned to Farbenfabriken Bayer AG, Germany is an improved process of manufacturing sulfuric acid.

Metallgesellschaft AG

A process developed by E. Stahl, U.S.Patent 2,819,947; January 14, 1958; assigned to Metallgesellschaft AG, Germany relates to an improved method of supplying the water necessary to bind the sulfur trioxide to form sulfuric acid.

A process developed by H. Drechsel, K.-H.Dorr, and H. Grimm ; U.S. Patent 3,404,955; October 8,1968; assigned to Metallgesellschaft AG, Germany is one in which gases having a sulfur dioxide content of less than 9 % are catalytically oxidized to SO_3 and H_2SO_4 in a method in which no external source of heat is employed.

Another process developed by H. Drechsel, K.-H. Dörr, and H. Grimm ; U.S. Patent 3,525,586; August 25, 1970; assigned to Metallgesellschaft AG, Germany is one in which gases having an SO_2 content of at less 9 % are catalytically oxidized to SO_3 and H_2SO_4 by using a plurality of heat exchange and oxidation steps and a hot single stage intermediate SO_3 absorption step.

Pullman

A process developed by L.E. Bostwick and B.G. Mandelik; U.S. Patent 3,432,264; March 11, 1969; assigned to Pullman Incorporated is a process for the manufacture of sulfuric acid where dynamic gas-liquid contacting means are used in place of conventional sulfuric acid to dry the air and are preferably also used in place of conventional packed towers to contact sulfur trioxide with sulfuric acid to form additional sulfuric acid.

Societe Nationale des Petroles d'Aquitaine

A process developed by H. Topsoe and G.Thareau; U.S. Patent 3,374,061; March 19, 1968; assigned to Societe Nationale des Petroles d'Aquitaine, France involves the manufacture of sulfuric acid by absorbing a hot humid gaseous stream containing sulfuric oxide in an aqueous sulfuric acid solution, the volume and concentration of which are maintained constant throughout the process.

Stauffer Chemical

A process developed by A. Belchetz ; U.S. Patent 2,449,190; September 14, 1948; assigned to Stauffer Chemical Company is unique in that it proposes the use of a fluidized bed catalyst.

UNCONVENTIONAL SULFURIC ACID PROCESSES USING LIQUID PHASE OXIDATION OF SULFUR DIOXIDE

Tennessee Valley Authority

A process developed by M.M. Striplin, Jr., U.S. Patent 2,342,704; February 29, 1944; assigned to Tennessee Valley Authority involves making an aqueous solution of sulfuric acid from sulfur dioxide by passing through a gas absorbing zone a stream of an aqueous absorbent solution containing mangenese sulfate and material selected from the group consisting of alkyl naphtalene sulfonic acids and the alkali metal salts, both in relatively small amounts and in the concentration required for the maximum rate of conversion for the concentration of the aqueous solution of sulfuric acid being produced.

USING LIQUID PHASE OXIDATION OF SULFUR

Sterling Drug

A process developed by E.W. Schseffel; U.S. Patent 3,042,489; July 3, 1962; assigned to Sterling Drug Inc. is a non catalytic process for the production of sulfuric acid in high yield by oxidizing sulfur in an aqueous dispersion to sulfur trioxide at a temperature between amout 275° and 360°C and under a pressure sufficient to maintain some of the water in liquid phase and recovering sulfuric acid from the oxidized product.

APPENDIX G

INTERNATIONAL PATENTS RELATED TO REMOVAL AND RECOVERY OF SULFUR OXIDES FROM TAIL GASES (133)

Types of systems available :

1.1.1	Dual Absorption
1.2.1	Add-on Dual absorption using converter heat
1.2.2	Add-on Dual absorption using furnace heat
1.2.3	Add-on Dual absorption using outside heat source
1 3.4	SO_2-SO_3 conversion improvement
2.1.1	Na_2CO_3 absorption of SO_2 to Produce Na_2SO_3
2.2.6	MgO absorption of SO_2 with SO_2 recovery
2.2.8	Potassium sulfite-Bisulfite
2.2.14	SO_2 absorption in and recovery from methylamine sulfite-bisulfite solution
2.2.22	Absorption and oxidation of SO_2 in charcoal beds (sulfacid process)
2.2.28	Absorption with basic aluminum sulfate solution, regeneration with heat to release SO_2 (Hardman-Holden)
2.2.29	Resin adsorption of SO_2
2.3.3	Lime absorption of SO_2

2.4.5 Ammonium sulfite-bisulfite absorption with SO_2 recovery and NH_4NO_3 production

2.4.6 Sulfuric acid-lime 2-stage absorption to recover SO_2 and produce plaster of Paris.

Process 1.1. - Dual Absorption (New Plant)

Description : Similar to conventional contact plant up to conversion step. Absorption of SO_2 takes place after 2 or 3 conversion stages; SO_2 gas is reheated and returned to the converter for additional conversion and acid recovery in a second absorber. There are several variations depending upon conversion requirements and plant steam system.

Recovers : SO_2 in the form of product H_2SO_4 for sale.

Status : In commercial operation

Licensor : Bayer

Applications : Reduced SO_2 emission from new sulfur burning contact plants

Control level Obtainable: To 500 ppm for SO_2; no mist control

Expected relative cost : Capital cost--average to high; operating cost--low.

Reliability : Same as modern contact plant

Estimated Overall Worth: Good, Feasible-shows enough potential to warrant further evaluation.

Process 1.2.1 Add-on Dual Absorption Using Converter Heat

Description : Stack gas is heated utilizing a part of the heat of reaction from the converter. This gas is blown through a new secondary converter and absorber to produce additional acid product.

Recovers : SO_2 in the form of product H_2SO_4 for sale.

Status : Current technology, beeing offered commercially.

Licensor : Chemico.

Applications : Reduce SO_2 emission from sulfur burning contact plants.

Control level obtainable: 500 ppm for SO_2: no mist control.

Expected Relative Cost : Capital cost-average, operating cost-low.

Reliability : Good. Equal to existing plant.

Estimated Overall Worth: Good. Feasible where space is available. Shows enough potential to warrant further evaluation.

Process 1.2.2 -Add-on Dual Absorption Using Furnace Heat

Description : Stack gas is heated with hot furnace gas obtained by burning additional sulfur in the sulfur furnace, which by passes the boiler system and first converter. The additional SO_2+Stack gas is converted to SO_3 in a new two-stage secondary converter, and passes through a secondary absorber to provide additional acid product.

Recovers : SO_2 in the form of product H_2SO_4 for sale.

Status : Current technology being offered commercially.

Patents : Applied for.

Licensor : Chemico.

Applications : Reduce SO_2 emission from most sulfur burning contact plants to 500 ppm.

Expected relative cost : Capital cost-average; operating cost--low.

Relability : Good-equal to existing plant.

Estimated overall Worth: Good. Feasible where space is available. Additional production limited by furnace and blower capacity of existing plant. Shows enough potential to warrant further evaluation.

Process 1.2.3 -Add-on Dual Absorption Using Outside Heat Source

Description : Stack gas is heated in a fired heater and blown through a new secondary converter and absorber to produce additional product acid.

Recovers : SO_2 in the form of product H_2SO_4 for sale.

Status : Current technology.

Applications : Reduce SO_2 emission from wet gas contact plants.

Control level Obtainable : 500 ppm for SO_2; no mist control.

Expected Relative Cost : Capital cost-average; operating cost-average.

Reliability : Good-equal to existing plant.

Estimated Overall Worth: Fair. May be feasible for some wet gas plant. Shows enough potential to warrant further evaluation.

Process 1.3.4 - SO_2-SO_3 Conversion Improvement

Description : Recently constructed contact H_2SO_4 plants can attain higher conversions either by restricting production rate or by additional catalyst.

Recovers : SO_2 in the form of H_2SO_4 for sale.

Status : Standard practice wherever applicable.

Applications : For contact plants that already achieve over 96 % conversion, to achieve 2,000 ppm, improvement for any contact plant.

Control level obtainable : Will have to be determined individually. Improvement to 2,000 ppm can be expected.

Expected Relative Cost : Capital Cost-variable (should be on low side); operating cost-very low.

Reliability : No change in reliablity of existing plant.

Estimated Overall Worth : Very good. Feasible for minor emission adjustments to most plants. Warrants further discussion.

Process 2.1.1 -Na_2CO_3 Absorption of SO_2 to Produce Na_2SO_3

Description : SO_2 is absorbed in a concentrated sodium sulfite solution made alkaline with sodium carbonate. A bleed stream is indirectly heated with by-product steam from the acid plant in a scraped surface crystallizer. The crystal slurry is centifugal and the crystals dried through indirect heat.

Recovers : SO_2 in the form of Na_2SO_3 crystals for sale.

Status : Pilot stage for SO_2 absorption; theoretical for crystallization.

Patents : Chemico application for SO_2 absorption and crystallization in venturi.

Application : SO_2; or SO_2, SO_3 and acid mist removal for most contact plants.

Control level obtainable : $<$ 100 ppm overall.

Expected Relative Cost : Capital cost-average; operating cost-high-if sodium sulfite value is significantly less than soda ash.

Reliability : Does not affect reliability of acid plant.

Estimated Overall Worth : Good, if sodium sulfide value is significantly greater than soda ash. Sulfate formation can be controlled and by-product steam from acid can be utilized. Feasible. Shows enough potential to warrant further evaluation.

Process 2.2.6-Magnesium Oxide Absorption of SO_2 with SO_2 Recovery

Description : SO_2 is absorbed in a magnesium sulfite-oxide slurry. The bleed stream is centrifuged. The hydrated salt is dried and the anhydrous sulfite calcined to magnesium oxide and SO_2. The SO_2 gas is scrubbed and the gas cooled and most of the water condensed before recycle to the 93 % tower.

Recovers : SO_2 in the form of concentrated gas for recycle to acid plant

Status : Diloted, and full-sized systems proposed. A variation in commercial use in pulp industry.

Patents : Several.

Applications : SO_2; or SO_2 and acid mist recovery from most contact plants.

Control level obtainable : About 100 ppm.

Expected Relative Cost : Capital cost-average; operating cost- average,

Reliability : Operates independently. Does not affect reliability of acid plant.

Estimated Overall Worth: Good. Feasible--shows enough potential to warrant further evaluation.

<u>Process 2.2.8-Potassium Sulfite-Bisulfite</u>

Description : SO_2 is absorbed in a $KHSO_3$-K_2SO_3

solution. The bleed stream is cooled precipitating potassium pyrosulfite which is separated, the redissolved and steam is stripped to K_2SO_3, releasing SO_2 which is cooled to condense moisture then cycled to the acid plant. The sulfite formed is recycled to the scrubbers. Sulfates can be removed from the system with lime, or removed prior to absorption, plus using an oxidation inhibitor with the sulfite-bisulfite solution.

Recovers : SO_2 in the form of concentrated gas for recycle.

Status : Commercial scale unit under construction.

Patents : Many on this type of process.

Applications : Most sulfur and non sulfur contact plants for recovery of SO_2.

Control level obtainable : $<$ 100 ppm overall.

Expected relative cost : Capital cost-high, operating cost-average.

Reliability : Operates independently.

Estimated overall worth : Good-Steam consumption 9 lbs/lb.SO_2 for vacuum crystallization and steam stripping. Feasible. Shows enough potential to warrant further evaluation,

Process 2.2.14 –SO_2 Absorption in and Recovery from Methylammonium Sulfite-Bisulfite Solution

Description : SO_2 is absorbed in methylammonium sulfite-bisulfite in two stages. A bleed stream containing the equivalent methylammonium bisulfite is steam stripped producing methylammonium sulfite and releasing SO_2. The former is returned to the scrubber and the SO_2 cooled to about 100°F to condense most of the H_2O before cycling to the acid plant. An oxidation inhibitor is added to the absorbing solution to reduce sulfate formation. Acid mist and SO_3 are scrubbed out prior to absorption.

Recovers : SO_2 in the form of concentrated gas for recycle.

Status : Johstone test data. Should be piloted.

Patents : Possible Jonhstone Patent about 1940.

Applications : SO_2; or SO_2, SO_3 and acid mist recovery from most contact plants.

Control level obtainable: As low as 100 ppm overall.

Expected relative cost: Capital cost-average, operating cost-average.

Reliability : Does not affect reliability of acid plant.

Estimated overall worth: Good. Steam requirements for desorption are a little high (18 lbs/lb SO_2). Methylamine vapor pressure in methylammonium sulfite-bisulfite is negligible at absorption temperatures. Feasible. Shows enough potential to warrant further evaluation.

Process 2.2.22-Absorption and Oxidation of SO_2 in Charcoal Beds

Decsription : SO_2 removed from various industrial waste gases. SO_2 converted to H_2SO_4 by wet catalysis. Product acid is 10+% H_2SO_4.

Recovers : SO_2 in the form of H_2SO_4 for sale, reuse as scrubbing liquor concentration, or possible recycle to acid plant.

Status : In use.

Licensor : Lurgi Gesellschaft Für Chemie und Hutenwesen GmbH.

Applications : SO_2, SO_3 and acid mist recovery from most contact plants; most economical when applied to plants with low SO_2 emission level.

Control level obtainable : $<$ 500 ppm.

Expected relative cost : Capital cost-Installed cost \$ 225,000 in Europe for 400 STD H_2SO_4 Plant, 1800 ppm emission. Operation cost - low.

Reliability : Does not affect reliability of acid plant.

Estimated Overall Worth : Not the most feasible unless there is a proper water balance since a 10 % acid is produced. Economical applications may be limited in U.S. Shows enough potential to warrant further evaluations.

Process 2.2.28-Absorption with Basic Aluminium Sulfate Solution, Regeneration with Heat to Release SO_2 (Hardman Holden)

Description : Sulfuric acid tail gas is scrubbed with a basic aluminium sulfate solution. SO_2 is recovered by steam and recycled to the drying tower. SO_3 and acid mist must be removed before scrubbing.

Recovers : SO_2 in the form of concentrated gas for recycle.

Status : In commercial operation (Europe), for SO_2 production from sulfur.

Patents : Many; U.S., British, German, Australian.

Licensor : Hardman Holden Ltd.

Applications : SO_2 recovery from any contact acid plant.

Control level obtainable: 500 ppm or lower for SO_2 and mist.

Expected Relative Cost : Capital cost-low, operating cost-average.

Reliability : Does not affect reliability of acid plant.

Estimated overall worth : Good. Feasible, but SO_3 and acid mist must be removed prior to scrubbing to minimize sulfate formation. Shows enough potential to warrant further evaluation.

Process 2.2.29-Resin Adsorption of SO_2

Description : SO_2 is adsorbed by an ion-exchange resin. The resin is regenerated with hot air. Acid mist removed just by decomposition with heat to H_2O and

SO_3, and SO_3 is absorbed by separate adsorbent.

Recovers : SO_2 in the form of SO_2 for recycle to the acid plant; removes SO_3 and acid mist.

Status : Laboratory developmet.

Patents : U.S. Patent pending for resin.

Licensor : Rohm and Haas (resin)

Applications : SO_2 recovery and acid mist removal from any contact acid plant.

Control level obtainable: 200 ppm or lower depending on regeneration cycle.

Expected relative cost : Capital cost-medium, operating cost-low.

Reliability : High, independent operation does not affect acid plant reliability.

Estimated overall worth: Good. Further development required for SO_3 removal step. Shows enough potential to warrant further evaluation.

Process 2.3.3-Lime Absorption of SO_2

Description : SO_2 is absorbed in a slurry containing hydrated lime. The bleed stream which contains mainly sulfites and sulfates is sent to a clasifier. The underflow is centrifuged and the solids sent to waste disposal. The supernatant liquid is recycled.

Recovers : Calcium sulfites and sulfates in the form of solids for disposal.

Status : In use on utility boilers in similar process.

Patents : Many.

Applications : Most sulfur and non-sulfur contact plants.

Control level obtainable: About 100 ppm, possibly lower.

Expected relative cost : Capital cost-low; operating cost -average to high.

Reliability : Operates independently.

Estimated overall worth: Good. if SO_2 emissions are relatively low and solid waste disposal facilites are available. Feasible. Shows enough potential to warrant further evaluation.

Process 2.4.5- Ammonium Sulfite-Bisulfite Absorption with SO_2 Recovery and NH_4NO_3 Production

Description : SO_2 is absorbed in two stages in solution of ammonium sulfite-bisulfite solution. Nitric acid is added to the ammonium sulfite-bisulfite bleed stream releasing SO_2 for recycle and forming ammonium nitrate. The ammonium nitrate in solution form is concentrated for sale. Ammonium sulfate formed is removed with the nitrate product.

Recovers : Concentrated SO_2 for recycle and ammonium nitrate for sale.

Status : In commercial operation in Europe.

Licensor : SCHZ (Czechoslovakia)

Applications : SO_2, SO_3 and acid mist recovery from most contact plants.

Control level obtainable : About 100 ppm overall.

Expected relative cost: Capital cost-high, operating cost-high.

Reliability : Operates independently. Does not affect reliability of acid plant.

Estimated overall worth: Good in locations where there is demand for NH_4NO_3 solution. Feasible. Shows enough potential to warrant future evaluation.

Process 2.4.6-Sulfuric Acid-Lime 2-Stage Absorption to Recover SO_2 and Produce Plaster of Paris

Description : SO_2 is absorbed in two stages. In the first, a 10 % H_2SO_4 solution containing $MnSO_4$ catalyst absorbs and oxidizes half the sulfur value entering the system. The remaining sulfur value is absorbed in the second stage with lime.

The acid is then reacted with the $CaSO_3$ product to form SO_2 which is recycled, and $CaSO_4.2H_2O$ which is calcined to $CaSO_4.1/2\ H_2O$.

Recovers : Concentrated SO_2 for recycle and plaster of Paris.

Status : Idea.

Patent : Russian # 50446 (1937).

Applications : SO_2,, SO_3 and acid mist recovery for most contact plants.

Control level obtainable : $<$ 100 ppm overall.

Expected relative cost : Capital cost-average, operating cost-average too high.

Reliability : Operates independently. Does not affect reliability of acid plant.

Estimated overall worth: Good. Shows enough potential to warrant further evaluation.

APPENDIX H

INTERNATIONAL PATENTS RELATED TO RECOVERY OF ACID MISTS(133)

Sulfuric acid mist consists of small drops of sulfuric acid, usually over 90 % concentration, formed in the vapor phase from water ~~vapor~~ and SO_3. Once formed it is extremely stable and is not readily separated or absorbed.

In spite of the precautions taken, some mist formation does take place in most plants. This may result from the inadequate performance of the drying tower or moisture in the sulfur, but the most common cause is the presence of hydrocarbons in the sulfur which burn with it producing water which will combine with SO_3 as the gas cools in the economizer or absorption tower. This mist formation may be accentuated by sudden drilling of the gas on cold surfaces, an effect sometimes produced by rain on the gas duct. This type of mist consists of sulfuric acid drops of between 1 and 5 microns.

A most persistent form of this mist is produced in most oleum plants. The important fact from a pollution stand point is that this mist consists of very much finer (0,2 to 3.0 micron) particles than that present in the normal mist produced in plants where oleum is not a product.

In a discussion of acid mist it is important to distinguish between it, gaseous SO_3 and sulfuric acid vapor. At the temperatures in an acid plant SO_3 is a colorless gas and, therefore, invisible. If present in the stack gas of an acid plant, as a result of poor absorber operation, it will combine with water vapor in the atmosphere when it leaves the stack and become a visibles mist. The only way of preventing this mist formation is to ensure that the SO_3 content of the gas leaving the absorber is vey low, by proper design and operation of the tower. The stack gas leaving the absorption tower will always contain sulfuric acid vapor as it will be in substantial equilibrium with the absorber acid. The only way this can be reduced is by cooling, and it may, in fact, condense in long ducts to the stack or in the stack itself, sometimes being carried out of the stack as relatively large droplets which fall in the vicinity of the plant. As operation of the absorption tower at low temperatures may make good absorption more difficult to achieve, it is clearly necessary to strike a proper balance between a high SO_3 content on the one hand and a high acid vapor content on the other.

Several processes which are feasible for SO_2 control will simultaneously provide control of acid mist and SO_3, either by choice or because the nature of the process requires the SO_3 and acid mist be removed prior to the removal of SO_2. The various feasible methods are:

3.1.1 Dual Pad Mist Separators
3.1.2 Tubular Type Mist Separators
3.1.3 Panel Type Mist Separators
3.2.1 Electrostatic Precipitation
3.3.1 Mist Removal with Venturi Scrubber.

System 3.1.1-Dual Pad Mist Separator

Description : Acid mist impinges on filaments of horizontal mesh pads located in top of the absorption tower to form large droplets which are returned to the tower by gravity.

Recovers : H_2SO_4 mist in the form of H_2SO_4 for sale as product.

Status : Many types in commercial operation.

Patents : Many.

Applications : Recovery of acid mist particles >3 microns from most acid plants not producing oleum.

Control level obtainable: Reduce acid mist to 2 mg/scf.

Reliability : High-does not affect acid plant reliability.

Estimated overall worth: Good. Feasible within its range of capability. Low gas velocities required.

<u>System 3.1.2-Tubular Type Mist Separator</u>

Description : Tail gas from the absorption tower passes through glass fiber packed vertical tubular elements. Recovered acid mist flows down the inside of the elements and is returned to the tower as liquid.

Recovers : H_2SO_4 mist in the form of H_2SO_4 for sale.

Status : In commercial operation.

Patents : Several.

Licensor : Monsanto (Brinks High Efficiency)

Applications : Recovery of acid mist for most acid plants.

Control level obtainable : Reduce acid mist emission to $<$0.1 mg/scf.

Expected Relative Cost : Capital cost-average, operating cost-low.

Reliability : High-does not affect plant efficiency.

Estimated overall worth : Good. Feasible-Can be accommolated within the absorber in new plants. Existing plants require separate units.

System 3.1.3 - Panel Type Mist Separator

Description : Tail gas from the absorption tower passes through vertical fiber panels into a chamber. Tail gas is discharged upward and collected mist as liquid is collected in a drain lime and returned to the absorber.

Recovers : Acid mist in the form of H_2SO_4 for sale.

Status : In commercial operation.

Patents : Several.

Licensor : Monsanto (Brinks High Velocity)

Applications : Acid mist recovery for most acid plants.

Control level obtainable: Reduce acid mist emission to <0.5 mg/scf.

Expected relative cost : Capital cost-low to average; operating cost-low.

Reliability : High-does not affect acid plant reliability.

Estimated overall worth: Good. Feasible-Can be accommodated within the absorber in new plants; existing plants require a separate unit.

System 3.2.1-Electrostatic Precipitation

Description : Tail gas is passed through a chamber with electrostatic element. Mist particles collect on the elements and fall as liquid to the bottom of the chamber and are returned to the acid plant.

Recovers : H_2SO_4 mist in the form of H_2SO_4 for sale.

Status : In commercial operation.

Patents : Many.

Applications : Acid mist recovery for most acid plants.

Control level obtainable : To 99 % mist removal. Near 100 % for <3 micron mist.

Expected relative cost: Capital cost-average to high; Operating cost-average to high.

Reliability : Good. Does not affect reliability of acid plant.

Estimated overall worth: Good. Feasible.

System 3.3.1-Mist Removal with Venturi Scrubber

Description : H_2SO_4 mist is entrained in a venturi scrubber operating at high pressure drop (30" to 40" H_2O). The scrubbing liquid may be water or H_2SO_4. The bleed stream can be neutralized with alkali and the salt disposed of if applied to a contact plant. This is not necessary with a concentrator.

Recovers : Acid mist in the form of $CaSO_4$ for disposal, or weak acid for concentration.

Status : Venturi scrubbers are in commercial operation on concentrators.

Patents : Many.

Applications : All acid plants except oleum for acid mist control.