

ELECTROCHEMICAL PRODUCTION OF MOLYBDENUM REFRACTORY
METAL POWDERS

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REFRACTORY METAL POWDERS**

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ABSTRACT

ELECTROCHEMICAL PRODUCTION OF MOLYBDENUM REFRACTORY METAL POWDERS

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Molybdenum (Mo) is a refractory metal and mostly used as an alloying agent in cast iron, steels and superalloys to enhance hardenability, strength, toughness and corrosion resistance. It also finds other uses either in the form of a pure metal or an element in, for example, lubricants and catalysts. Traditional metal production methods are not suitable for molybdenum because pure molybdenum has a very high melting point and tends to be oxidized at low temperatures. Hydrogen reduction of molybdenum oxide is a very common way for molybdenum production, but it has two stages during the process. In this study, an alternative method to produce molybdenum metal powder by electrochemical processes is studied. The experiments during this study are divided into two groups, which are using calcium molybdate, (CaMoO_4) and using molybdenum disulfide (MoS_2) as starting materials. CaMoO_4 powder used in the form of pressed pellets was reduced in molten CaCl_2 - NaCl mixture and it was found that most of CaMoO_4 dissolved in CaCl_2 - NaCl mixture. The experiments yielded 1.9% solubility by weight. MoS_2 powder pressed to form pellets were also used as starting material for electrochemical formation of pure molybdenum in molten CaCl_2 - NaCl salt mixture. Complete reduction of MoS_2 to molybdenum refractory metal powder was succeeded under argon gas flow at 750°C . A constant voltage of

2,8V was applied between graphite anode and cathode holding either CaMoO_4 or MoS_2 in all experiments.

Keywords: Electrodeoxidation, Molybdenum, Calcium molybdate, Molybdenum disulfide and Molten Salt Electrolysis

ÖZ

MOLİBDEN REFRAKTER METAL TOZLARININ ELEKTROKİMYASAL ÜRETİMİ

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Molibden (Mo) genellikle alaşım elementi olarak dökme demirlerde, çeliklerde ve super alaşımlarda sertleştirilebilirliği, dayanıklılığı, tokluğu ve korozyon direncini arttırmak için kullanılan bir refrakter metaldir. Ayrıca saf metal veya element halde yağlayıcı madde olarak ve katalizör olarakta kullanılır. Molibden çok yüksek erime noktasına sahip olduğu ve düşük sıcaklıkta oksitlenmeye yatkınlığından dolayı geleneksel metal üretim metotları molibden üretimi için uygun değildir. Molibden oksitin hidrojenle indirgenmesi molibden üretiminde çok yaygın bir yöntemdir fakat bu yöntem iki aşamaya sahiptir. Bu çalışmada geleneksel molibden üretimine alternatif bir yöntem olarak elektrokimyasal prosesle üretimi çalışılmıştır. Deneyler başlangıç tozu olarak kalsiyum molibdat (CaMoO_4) ve molibden disülfür (MoS_2) kullanımını olarak iki grupta yapılmıştır. CaMoO_4 tozu pelet formunda kullanılmıştır ve CaCl_2 - NaCl karışımı içinde indirgenmiştir. CaMoO_4 tozunun çoğunluğunun CaCl_2 - NaCl karışımında çözündüğü anlaşılmıştır. Ağırlıkça %1.9 çözünürlük belirlenmiştir. MoS_2 tozu pelet formda elektrokimyasal saf molibden oluşumu için başlangıç malzemesi olarak kullanılmıştır. MoS_2 tozunun tümüyle refrakter molibden tozununa indirgenmesi 750°C de argon gazı altında başarıyla gerçekleşmiştir. Tüm deneylerde grafit anot ile katot arasında sabit 2.8 V uygulanmıştır.

Anahtar Kelimeler: Elektrodoksidasyon, Molibden, Kalsiyum molibdat, Molibden disulfür ve Eriyik tuz elektrolizi.

To my mother, Filiz...

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LIST OF ABBREVIATIONS

ABBREVIATIONS

1. ADM: Ammonium Dimolybdate
2. Mo: Molybdenum
3. MoO₃: Molybdenum Trioxide
4. CaMoO₄: Calcium molybdate
5. MoS₂: Molybdenum disulfide

CHAPTER 1

INTRODUCTION

Molybdenum (Mo) is a metallic element and mainly used as an alloying element in cast irons, steels and superalloys to improve hardenability, strength, toughness and corrosion resistance. In addition, it is used in pure metal or compound form for some applications such as a lubricating substance or an accelerator.

Molybdenum has one of the highest melting temperatures of all metals; however, the density of molybdenum is only 25% greater than that of iron, unlike other refractory metals which have very high densities. Despite having high thermal conductivity, it has very low thermal expansion coefficient. Furthermore, molybdenum-based alloys have high strength and high thermal and electrical conductivity. These properties make molybdenum and its alloys indispensable for special applications [1].

The demand of molybdenum and molybdenum based alloys for special practices makes the production of Mo continue at high levels. The production of molybdenum had increased noticeably in between 2010 and 2014. However, a sharp decrease in the production of molybdenum was seen in 2015. After this remarkable decrease, demand for molybdenum started to rise and production of molybdenum increased again and became 17 million metric tons in 2017 [2]. When the mine production of molybdenum in 2018 compared to 2017 and 2016, it can be figured out that there is an increase in U.S. Mines at Colorado which produces molybdenum as a primary product [3]. Mines in Montana, Nevada, Arizona and Utah provide recovered molybdenum from copper mines as a byproduct. There are also roasting plants in U.S to produce molybdenum oxide as an intermediate product.

Nowadays, top four countries produce 90% of the world's total needs for molybdenum. China is unmatched the leader of this supply with a large difference between other countries contributions and its own. Chile is the second largest producer of molybdenum in the world. Provider of the molybdenum products in Chile is a state owned company called Codelco.

Classical Molybdenum processing contains many steps: crushing, grinding, flotation and leaching after mining. After the collection of concentrate, it still needs the enhancing processes [4]. Basically the enhancement process to produce pure MoO_3 is based on chemical treatments and calcination processes. The purity level of MoO_3 has to be at least 99.95% for use in chemical starting materials, which are ammonium molybdate (ADM) and sodium molybdate. They are produced by reacting chemically pure MoO_3 either in aqueous ammonia or sodium hydroxide. Besides the metallic molybdenum powder, ammonium molybdate is used for the preparation of molybdenum chemicals or catalysts.

Metallic molybdenum is produced by the hydrogen reduction process of pure molybdenum trioxide (MoO_3) or ammonium dimolybdate (ADM). The process is carried out in electrically heated tubes of muffle furnaces. The hydrogen gas meets as counter current against the supply. Mainly, there are two steps which are formation of pure molybdenum dioxide from pure molybdenum trioxide or AMD and formation of pure molybdenum powder from pure molybdenum dioxide for production of Mo metallic powder from MoO_3 or ADM to metal powder. Although hydrogen reduction process is the only commercial way to produce Mo metal powder, it has certain disadvantages.

1.1. Aim of This Study

In this study, it is aimed to find an alternative method to produce molybdenum metal powder by an electrochemical process apart from commercial production process of molybdenum metal which involves hydrogen reduction. Also, it is targeted to find a suitable molybdenum based raw material for production of molybdenum refractor

powder. Since there is very limited literature on production of Mo powder by electrochemical methods, results of the study will directly contribute the literature.

CHAPTER 2

LITARATURE REVIEW

2.1. THE ELEMENT OF MOLIBDENUM

Molybdenum is a very hard transition metal with symbol Mo and has an atomic number 42. It has very high melting point and very low thermal expansion coefficient. However, its density is only a quarter time greater than iron, unlike other high melting point metals which have very high densities.

Molybdenum is an important alloying element especially for steel and cast iron. It improves strength, hardenability, weldability, and toughness and corrosion resistance. Also, it contributes the resistance of corrosion and high temperature creep deformation in nickel based alloys. Moreover, most molybdenum based alloys have high strength, high thermal and electrical conductivity and low thermal expansion [6]. Some properties of molybdenum are given in Table 2.1.

Table 2.1. *Properties of Molybdenum*

Atomic number	42
Atomic weight	95.96
Crystal structure	Body-centered cubic (BCC)
Lattice constant	$a = 3.1470 \text{ \AA}$
Density	10.22 g/cm^3
Melting temperature	2623°C
Coefficient of thermal expansion	$4.8 \times 10^{-6} / \text{K}$ at 25°C
Thermal conductivity	138 W/m K at 20°C

Molybdenum has a large variety of valence and many complex compounds as a transition element. Chemically variety of molybdenum is outstanding such as oxidation state changing between 2^- to 6^+ and coordination number in between 4 to 8. As a result of this, it is able to form compounds with organic and inorganic ligands with oxygen, sulphur and chlorine atoms [7].

Molybdenum properties are very close to tungsten which is another member of group 6 of periodic table. However, they are not similar to chromium which is also at same group in periodic table.

Molybdenum metal is generally used for producing parts by powder metallurgy. Hydrostatically compacted Mo powder is sintered at around 2100°C then hot working is applied around $870\text{-}1260^\circ\text{C}$. Mo forms a volatile oxide when heated in air above about 600°C and; therefore, high temperature applications are limited to non-oxidizing or vacuum environments [8].

2.1.1. History of molybdenum

Molybdenum comes from ancient Greek name molybdos meaning lead like. Most abundant Mo-containing mineral is, molybdenite, MoS_2 , which was in this class along with lead, graphite and galena. In history, molybdenum as an alloying element was used in Japanese swords in the 14th century. Molybdenite was first found in sulphide compounds as an undefined compound in 1768 by the Swedish scientist Carl Wilhelm Scheele. He decomposed the compound in nitric acid, and then heated it in open air and got white oxide powder. After that, Peter Jacob Hjelm produced the dark metal powder by chemically reducing oxide following Scheele's study in 1782.

In the late of 19th century molybdenum was studied in lab scale, after commercial extraction processes became practical. Experiments showed that adding molybdenum element in steel instead of tungsten was really effective. Mo was used as an alloying element first in 1891 by Schneider & Co. the French company [9].

There was an increase in demand of tungsten in parallel with the sharp increase in demand of alloy steel during the World War I. As a result of this, molybdenum became more popular because it could substitute tungsten. This demand on molybdenum promoted the studies about it. In 1918, Climax deposit in Colorado, USA was found. Demand of molybdenum was decreasing after the war; therefore, studies and researches about application of molybdenum on new usage areas began. As a result of new researches, low alloy molybdenum steels for automobiles were developed. During 1930s, proper temperature ranges for forging and heat treatment of molybdenum were determined. Molybdenum became a technical material at the end of the 1930s [10].

During World War II, molybdenum became an important substitute element for tungsten in alloys. Molybdenum containing alloys and steels became popular markets for civilian applications after the war [10]. Nowadays, molybdenum is important not only for steels and cast irons but also for superalloys, nickel based alloys, lubricants, chemicals and electronics.

2.1.2. Source of molybdenum

Molybdenum trioxide, MoO_3 , sodium molybdate Na_2MoO_4 , ammonium heptamolybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{Mo}_7\text{O}_{24}\cdot 2\text{H}_2\text{O}$ are the typical compounds for molybdenum oxide. Most common and stable molybdenum compounds are molybdenum (III) oxide, MoO_3 , molybdenum dioxide, MoO_2 , and molybdenum disulphide, MoS_2 , which is a natural form of molybdenum.

Normally molybdenum has four forms of sulphides which are MoS_3 , MoS_2 , Mo_2S_5 and Mo_2S_3 . Industrially molybdenum trisulfide, MoS_3 , and molybdenum disulfide, MoS_2 are used. Besides being a natural source of molybdenum, MoS_2 , might be synthetically produced by heating higher sulphides with no air and melting MoO_3 with soda and sulphur [11].

Molybdenum reserves are computed around 17 million metric tons in 2017 as the world total reserves. The largest molybdenum reserves belong to China with around 8.3 million metric tons, which means that 48.8% of world's total reserves of molybdenum are in China [2]. The US is following China as the second big source for molybdenum with nearly 2.7 million metric tons molybdenum reserves. Turkey has around 0.7 million metric tons of molybdenum reserves which corresponds to 4% of total molybdenum world reserves. The reserves of Chile and Turkey were reported by the government and companies [2].

2.1.3. Pricing

Molybdenum oxide price with respect to years from 2000 to 2010 was given in the literature [8]. Molybdenum oxide prices had a sharp decrease at the beginning of 2009 due to less demand for it; however, with the China's contribution, molybdenum prices started to rise in 2009 [8]. Price fluctuations of molybdenum oxide with years are given in Figure 2.1.

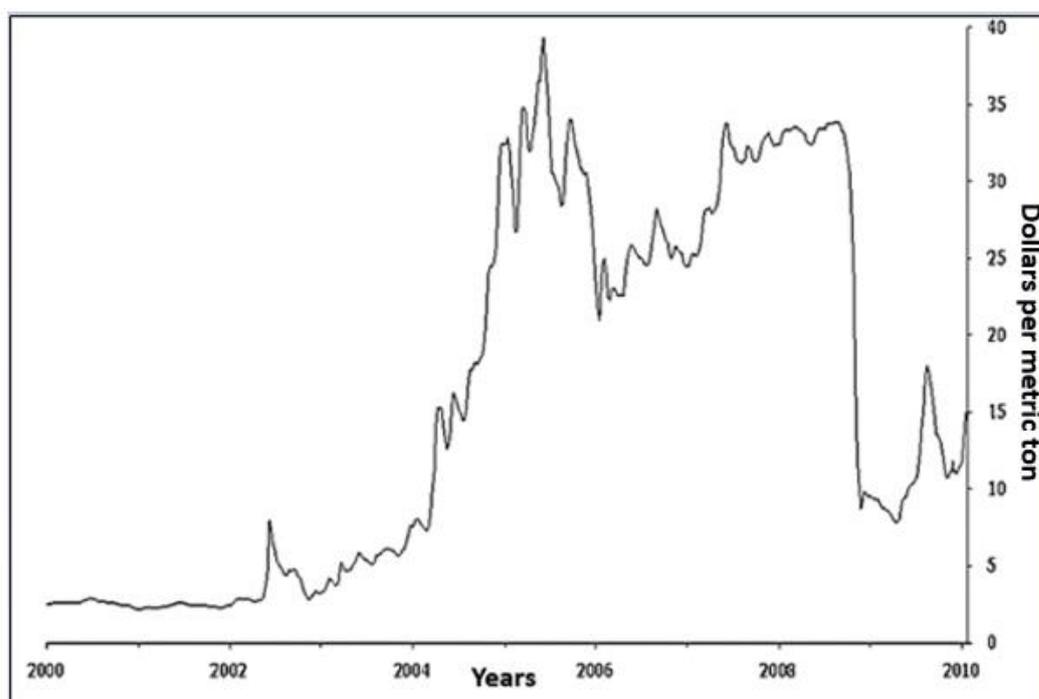


Figure 2.1. Mo Oxide Price in dollars per pound in between 2000 and 2010. Retrieved from [8].

Between years 2012 and 2018 molybdenum oxide price distribution is shown in Figure 2.2. In 2018, price raised to 16.8 US dollars per kg with demand for stainless steel and oil and gas industry. Production of molybdenum for steel industry was the main consumption part so that current year metal demand was %18 higher than previous year. On the other hand, oil and gas industry was rapidly expanding sector for four years to increase molybdenum demand.

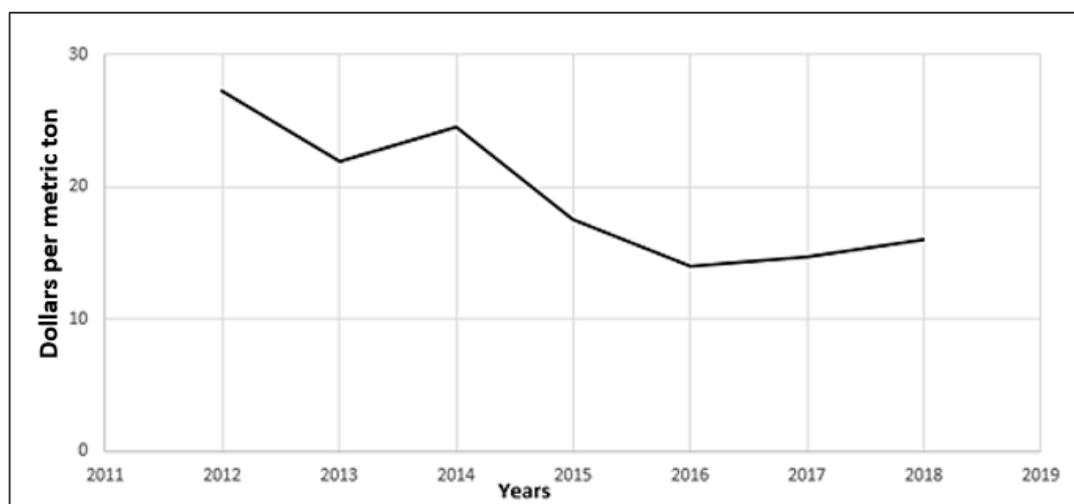


Figure 2.2. Mo oxide price in dollars per metric ton between years 2010 and 2018. Retrieved from [8].

2.1.4. Application Areas

Molybdenum is generally used as an alloying element in steels, cast irons and superalloys to enhance properties such as hardenability, strength, corrosion resistance and toughness. Although today there is a wide range of application areas for molybdenum, it was used only for lamp sector in the past [7].

Molybdenum compounds have important technological applications such as use of molybdenum disulfide and sulfur complexes as lubricant additives, corrosion inhibitors, smoke suppressants and molybdenum trioxide and molybdates as heterogeneous catalysts. Furthermore, in recent years, molybdenum compounds were

tried to replace toxic metal compounds like chromium in corrosion inhibitors and antimony because of their nontoxic nature [7].

For high temperature applications, it has been used for ceramics, high melting metals and superalloys. Moreover, because of its high failure tolerance, molybdenum is used for thermal radiation shields and some furnace components, especially in sintering furnaces. Due to the fact that molybdenum is a corrosion resistant material, it is also used for producing glass in glass melting furnace [3].

For the electronic applications, molybdenum is used for power transistors as a disk form. Also, it is an integral compound for belching as a target material. Mostly as a form of MoSi_x , the films are manufactured by the co-deposition from high purity molybdenum and silicon targets. The integrated circuits which have those films have low interference capacitances and have low input-output passage for current detention. This leads a manageable and consistent current distribution on semiconductor. Furthermore, components used in car engine include molybdenum as a form of layer which is produced by thermal spraying, thanks to its good sliding properties and high abrasion resistance [6].

Rotating X-Ray anodes mostly consist of molybdenum alloys which are around 80%. Charging parts might be improved by a thin layer of tungsten rhenium on a molybdenum body. Rhenium on this body is able to contribute to hinder propagation of cracks and increase ductility [15].

It is applicable and acceptable to use molybdenum in many different areas such as aerospace industry, automotive industry, energy, construction and electronics applications owing to its magnificent properties. Some application areas of Mo are given in Figure 2.3 [2].

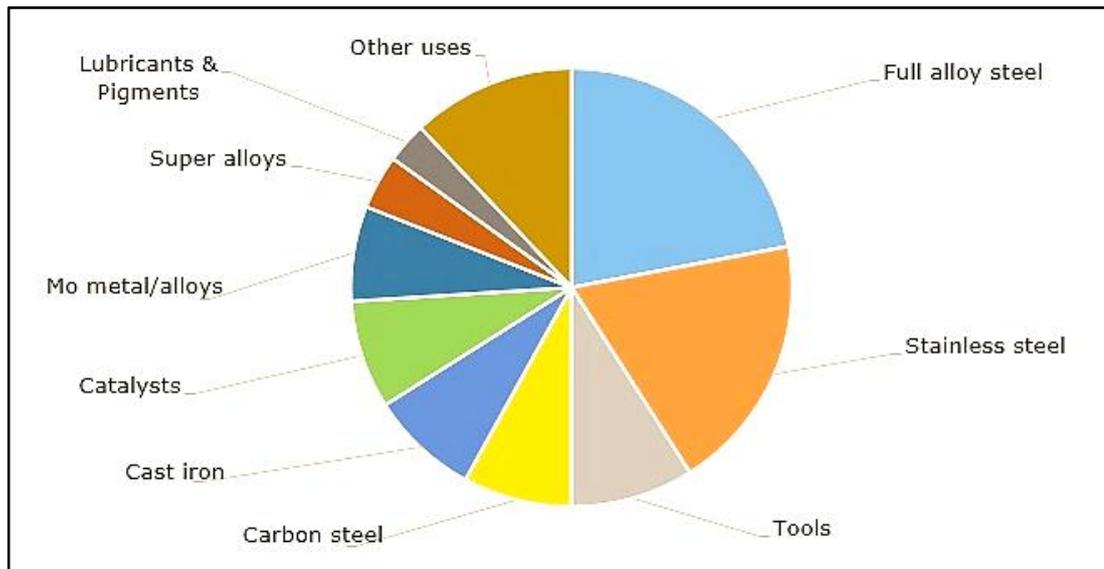


Figure 2.3. Application areas of molybdenum. Retrieved from [2].

2.2. Production of Molybdenum

2.2.1. Production of Mo Concentrate by Recovery Processes

Primary molybdenum ores mined as an ore body contains almost 0.05-0.25% Mo. It is preferred to produce industrial grade molybdenite concentrate by flotation of upgraded molybdenite mineral. Flotation steps start with pulverization in order to gain molybdenite from ore body. Rinsing the pulverized ore with water or special chemicals is the following part. Copper and molybdenum in the ore body are present as the unwetted part so that they can remain on the surface via air bubbles then and rest stays suspended as wet particles. Some private agents are used to gather air bubbles together with copper and molybdenum minerals from the surface.

Primary ore flotation is quite different from secondary ore bodies because flotation of molybdenite is named as natural floaters because of the spontaneity of the process [13]. Primary molybdenite recovery process is schematically seen in Figure 2.4.

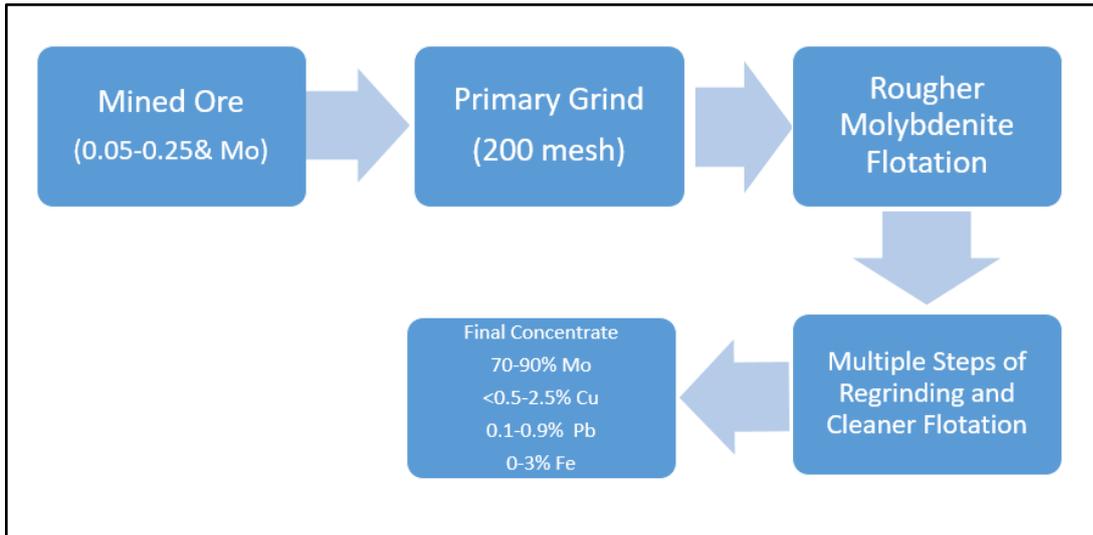


Figure 2.4. Flowchart of the primary molybdenite recovery process

2.2.2. Production of Mo Concentrate by Recovery Processes from Secondary Ores

Flotation of copper-molybdenum sulphide concentrate is assumed as a feasible process for molybdenum recovery. After the process, molybdenum is gained by extraction from the final concentrate by splitting. Following this, grinding is applied to the copper molybdenum sulphide concentrate, and then, bulk flotation takes place. Then, using selective reagents, rougher molybdenite flotation is done to obtain regrinding and cleaner flotation for separating non copper from concentration circuit. Steps of the secondary molybdenite recovery process are given in Figure 2.5.

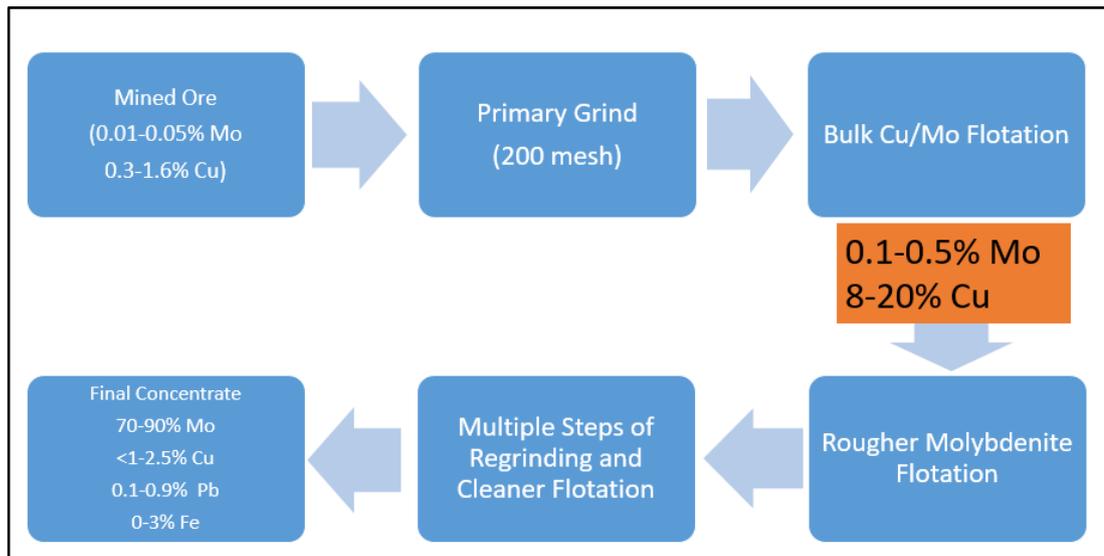


Figure 2.5. Flowchart of the secondary molybdenite recovery process

Molybdenum losses during bulk flotation are nearly 48% of total molybdenum in concentration mixture. With the redesign of systems and detected optimum values for copper recovery, it is expected to decrease the amount of molybdenum losses. Selective reagents used during molybdenite flotation are able to provide separation of molybdenum from concentration mixture consisting of molybdenum-copper. Grinding and cleaning steps are aimed to make separation of copper and molybdenite ore at desired levels.

2.2.3. Production of Molybdenum Trioxide

Primary product of the molybdenum is commercially called technical grade molybdenum trioxide which has many other common names such as molybdenum oxide, molybdenum (III) trioxide, molybdic oxide or molybdic acid anhydride [14]. Technical grade molybdenum oxide named as impure molybdenum trioxide contains 80% molybdenum trioxide, 6% molybdenum suboxides, 4% iron molybdates, 3% quartz, 1% calcium molybdate, 0.45% copper compounds, 0.03% lead compounds and 0.012% arsenic compounds [14]. During roasting of molybdenum (VI) sulphide, MoS_2 , to produce technical grade molybdenum trioxide, MoO_3 , multiple heart furnace

is used in an open atmosphere at around 650°C because the furnace is able to obtain specific operations in a single unit [11]. In the furnace, sulphur is mainly reacted with oxygen in the intermediate hearts [15].

During roasting, heat is produced because of the exothermic reactions of sulphur oxidation with the control of temperature by excess air. There are some other ways to produce molybdenum trioxide such as hydrometallurgical ways with solvent extraction and ion exchange.

To obtain molybdenum and ferromolybdenum alloys, molybdenum dioxide (MoO_2), ammonium dimolybdate (ADM), calcium molybdate or technical grade molybdenum trioxide is needed. Molybdenum trioxide also has an important part in steelmaking processes because it is reduced directly by liquid iron to the metal form. 80% of produced molybdenum from technical grade molybdenum trioxide is used in steel making [15]. For production of pure molybdenum oxide from technical grade molybdenum trioxide, ammonium dimolybdate is calcined by air [11].

For production of ammonium dimolybdate, as seen in Figure 2.6 from technical grade, MoO_3 , leaching is needed with heat to remove alkali impurities which are soluble. After the process, this oxide is dissolved in an ammonium hydroxide solution to get ADM [11].

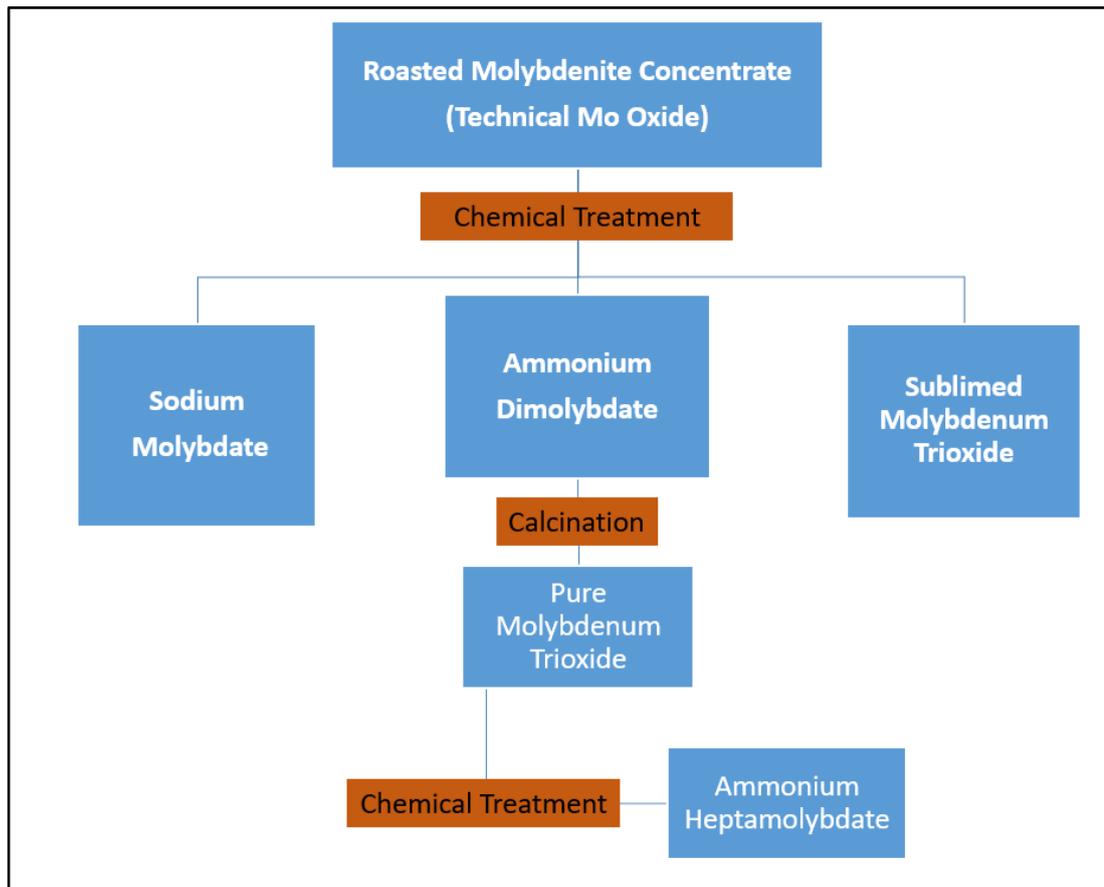


Figure 2.6. Flowsheet of production of pure molybdenum trioxide and AHM.

For the production of calcium molybdate and other molybdates from technical grade MoO_3 leaching is applied similar to ADM production process and calcium or other similar molybdates in hydroxide form are dissolved and calcium molybdate is precipitated [11].

2.2.4. Production of Mo Metal Powder

In order to obtain end products made of Mo metal, powder metallurgy processes should be applied. As a result of this, molybdenum concentrates are reduced to be pressed and sintered. This reduction is performed by hydrogen commercially. Firstly, molybdenum trioxide is reduced to molybdenum dioxide at the starting step. The second step is to reduce molybdenum dioxide to molybdenum metal powder as shown in Figure 2.7.

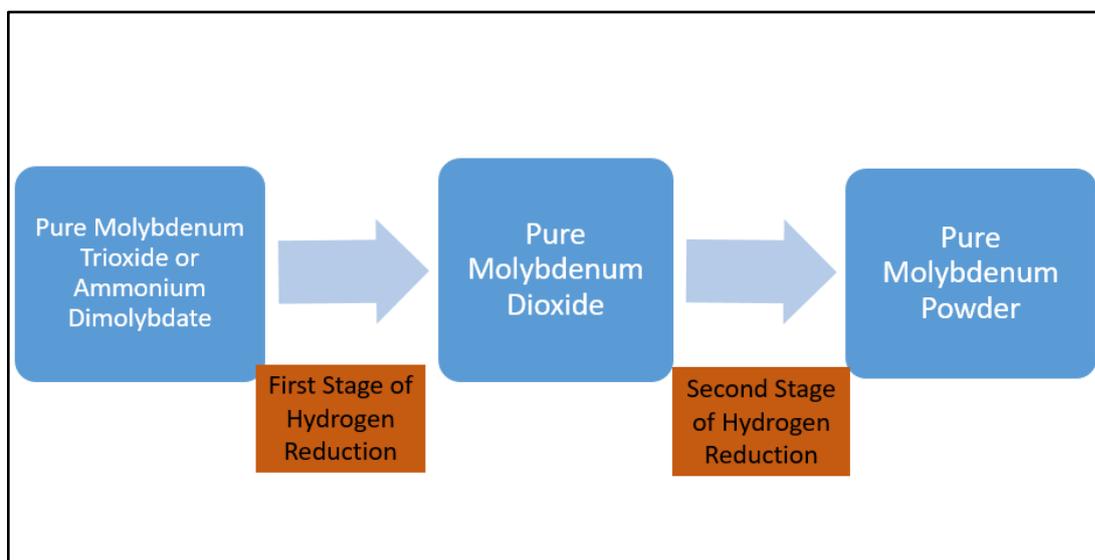


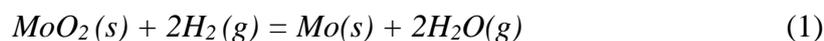
Figure 2.7. Flowchart of the production of molybdenum with hydrogen in two steps.

Reduction of MoO_3 to MoO_2 is performed at around 600°C to make sure there is no agglomeration because melting point of MoO_3 is 800°C . Second stage of the reduction process is performed at 1050°C . Both stages are conducted in fluidized bed reactors or electrical heated furnaces such as beam furnace, rotary kiln furnace etc. with stream of hydrogen.

For these reactions, hydrogen behaves like a reducing agent and leaves the system as water vapor by reacting with oxygen from oxides. In order to determine the particle grain size of produced molybdenum powder metal, it is important to concern temperature of reactions, flow rate of hydrogen and time for heating.

Although, hydrogen is a desirable reducing agent for production of molybdenum powder metal due to the fact that it provides high purity final product, it has some disadvantages like the high energy need, low driving force for reaction and it is not a safe gas to work with. The reduction processes have many sub reactions to reduce oxides to get metallic Mo powder which leads to extra energy requirement and prolonged processing time. In addition, Gibbs free energy difference is quite low

which results in low driving force for the reaction that is given in Equation (1). The values for standard Gibbs free energy change and enthalpy change for hydrogen reaction are also shown in Equation (2). Moreover, process needs extra heat from surroundings due to its endothermic nature.



$$\Delta G^\circ = -1.190 \text{ kJ mol}^{-1}, \Delta H^\circ = 71.558 \text{ kJ mol}^{-1}, (1100^\circ\text{C}) \quad (2)$$

2.3. Electrochemical Production of Metals

In the past, the only molten salt process with an oxide starting material was electrowinning of aluminum in Hall-Heroult process. During the process, alumina is first dissolved in cryolite, and then aluminum was obtained by passing through an electric current. Other metal extraction attempts for production of metals from their oxides by electrolytic reduction included dissolving the oxides in fluoride melts. The reason why these attempts could not produce a commercial process was because fluoride melts are very corrosive and produces undesired gaseous products [16].

Normally, alkaline earth chlorides dissolve in their oxides. However, generally most of the oxides do not dissolve in their own chlorides. As a result of this, electrowinning of these elements should be applied by dissolving the oxide in their chlorides [16].

In 1960s, Ward and Hoar [17] worked on molten copper purification that involved electrolytic removal of oxygen, sulphur, selenium and tellurium from an impure copper cathode. Molten barium chloride electrolyte and a carbon anode were used. It was shown by the results that it was possible to purify copper. Yet, the need for a large electrode area to treat the product was a problem against industrialization of the process. Furthermore, Ward and Hoar [17] reported that the mechanism of the process was diffusion controlled by the impurities in copper.

2.3.1. FFC Cambridge Process

Molten salt electrolysis is only applicable for low melting point metals. In order to obtain metals which have high melting points, an alternative electrochemical process is needed. In 1997, a research was done and it was about production of metals from their oxides directly in molten salt. It was named as FFC Cambridge Process coming from inventor's initial names (Fray-Farthing-Chen) [18]. Process was initially performed on solid oxide films on titanium foil as cathode in molten calcium chloride salt. Then, it was developed by using solid titanium oxide pellets to reduce it to the metal powder form [18]. The cell that was used in the process contained a graphite rod as the anode, metal compound pellets as the cathode and molten calcium chloride salt as the electrolyte that the schematic representation of the cell is given in Figure 2.8.

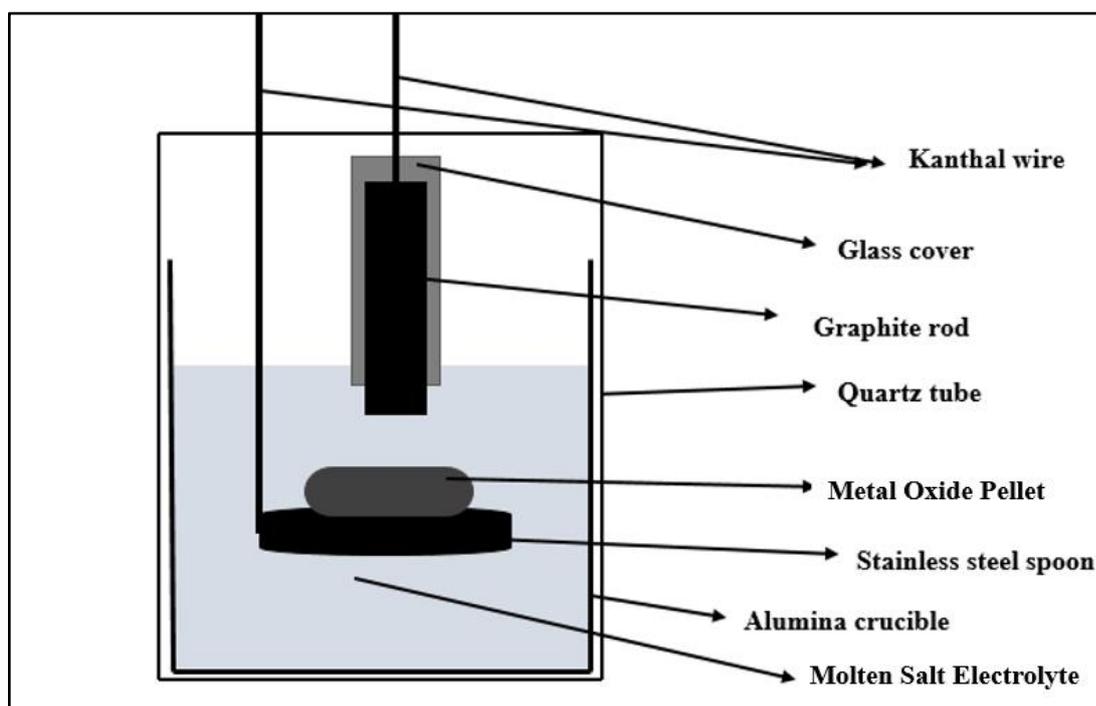


Figure 2.8. Schematic view of the FFC Cambridge Process cell.

A Potential difference that is lower than decomposition potential of molten salts and higher than decomposition of the metal compound was applied during the process.

Thanks to the applied potential difference, impurity ions formed a compound with carbon from graphite anode and cathode purity was provided. It was claimed that this process effective for especially high melting point metals. In the laboratory, a large number of metal oxides were reduced to the metals such as, W [23], Mo [16], Ti [19], Zr [19], Cr [20], Nb [20], Ta [20], U [21], Ni [21], Si [22], and Cu [23] by the electrodeoxidation.

2.4. Electrochemical Production of Molybdenum

Electrochemical production of molybdenum by classical molten salt electrolysis is not suitable because its melting point is very high so that dendritic formation problem occurs. An alternative method to produce molybdenum is to use FFC Cambridge Process. However, the studies on W [24] proved formation of gaseous WO_2Cl_2 while trying to reduce WO_3 at $900^\circ C$ by FFC Cambridge Process. FFC Cambridge Process was not suitable for W production because of W losses.

Since Mo has many similar properties with W, the system was studied using thermodynamic calculator FACT before starting the experiments [29]. It was observed that when MoO_3 and $CaCl_2$ comes in contact, they react to form $MoO_2Cl_2(g)$ and $CaMoO_4$ as seen in Figure 2.9. Therefore, reduction of MoO_3 in $CaCl_2$ containing molten salt by FFC Cambridge Process is not suitable without Mo loss similar to electrodeoxidation of WO_3 . Alternative starting material and produce for electrochemical Mo metal powder production is the subject of this thesis.

```

MoO3 + 5 CaCl2 =

0.50000 mol gas_ideal
(99.432 gram, 0.50000 mol, 41.029 litre, 2.4235E-03 gram.cm-3)
(1000 K, 1 atm, a=1.0000)
( 0.99998 MoO2Cl2
+ 9.5159E-06 MoCl4
+ 8.9395E-06 Cl2
+ 1.1552E-06 + 4.5000 mol CaCl2_Hydrophilite
+ 2.1735E-06 (499.43 gram, 4.5000 mol)
+ 2.5049E-06 (1000 K, 1 atm, S1, a=1.0000)
+ 1.5170E-1 + 0.50000 mol (CaO)(MoO3) Pawellite
+ 1.2517E-1 (100.02 gram, 0.50000 mol)
+ 1.7771E-1 (1000 K, 1 atm, S1, a=1.0000)
+ 9.1645E-1

```

Figure 2.9. Results of the FACT program for MoO₃ and CaCl₂ reaction. Retrieved from [29].

CHAPTER 3

EXPERIMENTAL

3.1. Experimental Procedure for CaMoO₄ and MoS₂ Starting Powders

Salt mixtures that were used in the experiments were dried before each experiment. For CaCl₂, a drying path was followed as shown in Table 3.1 in a high temperature furnace (Lindberg). For NaCl salt, 3 hours dwell time at 120°C was applied in a chamber at atmospheric pressure (Huve EV018).

Table 3.1. *Table of the temperature, rate and dwell time of drying path for CaCl₂ salt.*

<i>Temperature (°C)</i>	<i>Rate (°/dk)</i>	<i>Dwell time (hr)</i>
120	1	3
240	1	3
400	2	3
600	2	3

Figure 3.1 shows the schematic drawing of the experimental setup that was used in constant voltage experiments. 2 grams of MoS₂ powder (Aldrich, 1371634V) or 2.5 grams of CaMoO₄ powder (Alfa Aesar, 43686-E03R051) was pressed under 1.5 tons of load and used without sintering in all experiments. Average diameters and heights of porous pellets were measured as 15 mm and 5 mm, respectively. The pellet was placed into a stainless steel spoon which was used as the cathode contacting material for each experiment.

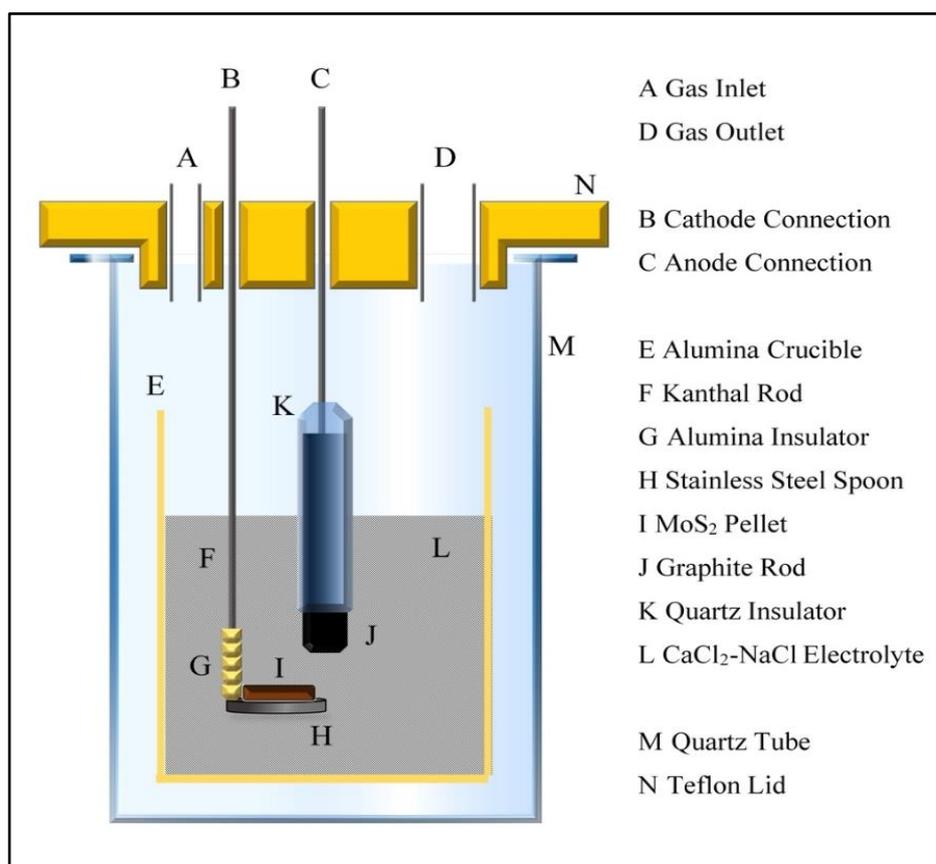


Figure 3.1. Schematic view of experimental set up.

A graphite (Alfa Aesar A10134) rod having 15 cm long and 13 mm diameter was used as the anode. It was attached to a 3 mm diameter stainless steel wire and extended out of the cell vessel to facilitate electrical contact to power source at around room temperature. Eutectic CaCl₂ (52 mole %) (Riedel-de-Haën 12022) and NaCl (48 mole %) (Riedel-de-Haën 13423) mixtures and CaCl₂ (70 mole%)–NaCl (30 mole %) mixtures were used as electrolytes. Experiment temperatures were chosen as 600, 750 and 900°C for CaCl₂–NaCl molten salt mixture depending on the phase diagram of CaCl₂–NaCl in order to indicate the liquid salt region. Phase diagram [40] is shown in Figure 3.2.

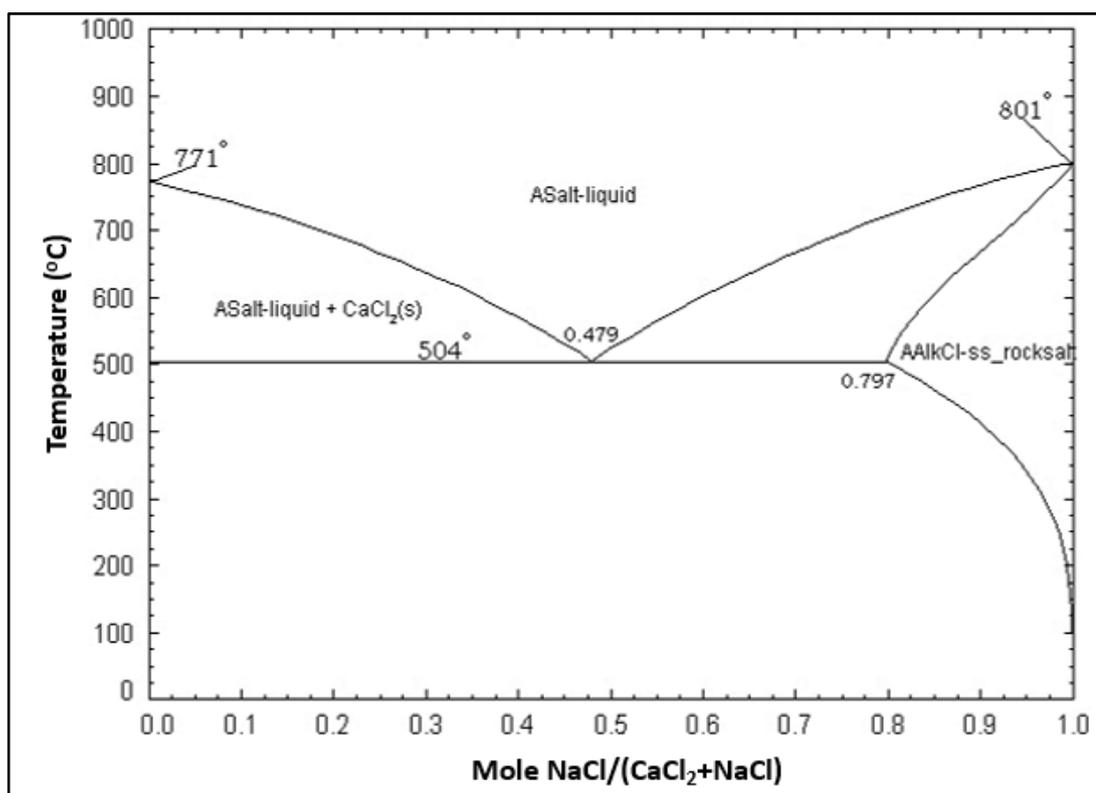


Figure 3.2. Temperature (°C) vs mole NaCl/ (CaCl₂+NaCl) Phase Diagram. Reproduced from [29].

The electrodes were immersed into the electrolyte and 2.8 V constant potential was applied via Agilent N6700B DC power supply. At the end of each experiment, reduced sample was washed with distilled water in ultrasonic mixer for 10 minutes. In addition, HCl treatment was applied in 0.1M HCl solution to remove calcium carbonate (CaCO₃) or other byproducts which were formed due to CO₂ evolution at anode and/or other constituents or byproducts of the process. The products were dried under atmospheric conditions and characterized by SEM, XRD and XRF methods which will be mentioned in part 3.

3.2. Experimental procedure for solubility of CaMoO₄

In this setup; alumina crucible, tungsten wire and tungsten plate were used as shown in the Figure 3.3. The same procedure was followed to form pellets having similar properties and specialties as explained previously to study the CaMoO₄ solubility in molten salt. 2 grams of CaMoO₄ powder (Alfa Aesar, 43686-E03R051) was pressed

under 1.5 tons of load. Average diameters and heights of porous pellets were measured as 15.6 mm and 5.3 mm, respectively. Pellet was placed onto a tungsten plate and it was immersed with tungsten wire into the electrolyte. No electrical connections were used. No voltage was applied. Electrolyte was composed of CaCl_2 (70 mole%)– NaCl (30 mole %) (Riedel-de-Haën 13423) mixture. A pellet was immersed into the molten salt mixture and allowed to stay there for 12 hours at 750°C . During this period, a sample was taken from salt after 3 hours 6 hours and 12 hours for compositional analysis.

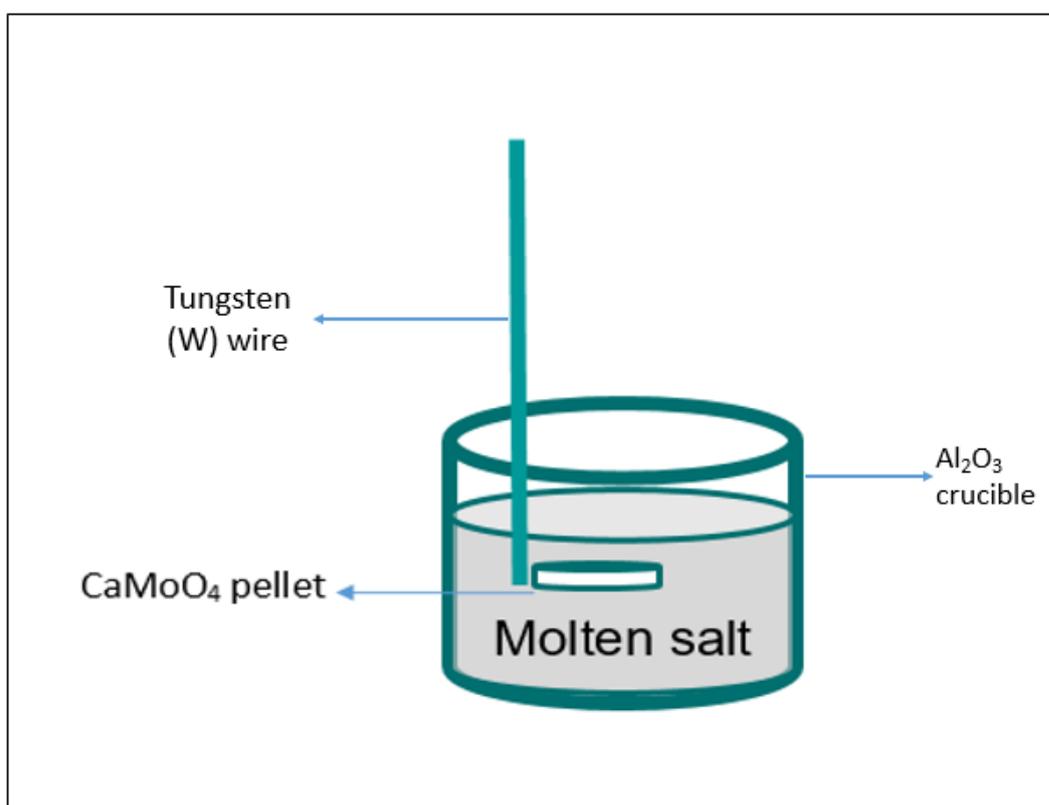


Figure 3.3. Schematic view of components used in solubility experiment.

3.3. Characterization

In order to characterize starting materials, intermediate and final product samples, scanning electron microscope (Nova NanoSEM 430), X-ray diffractometer (Rigaku D/Max2200/PC) and X-Ray Fluorescence (Bruker S8 Tiger) were used.

SEM were used in order to understand the shape and size of samples and to obtain their images. Also, energy dispersive system (EDS), that was part of Nova NanoSEM 430 scanning electron microscope, was performed to make elemental analyses.

XRD analyses were performed by Rigaku diffractometer via $\text{CuK}\alpha$ radiation at a wavelength of 0.154183 nm. In X-Ray diffraction method, a scan rate of $1^\circ/\text{min}$ and sampling width of 0.02° were used to obtain data from samples. Moreover, data were collected between 5° and 110° . The Rigaku qualitative analysis software was used to examine X-ray data to refine them.

XRF were performed to make elemental analysis of samples in this study. Energy dispersive system (EDXRF) was used as spectrometer system for elemental analysis. The resolution of the machine was 135 eV with $\text{MnK}\alpha$ radiation.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Electrochemical Reduction of CaMoO_4

It is not possible to produce Mo metal powder without any loss by the FFC Cambridge process. At the elevated temperatures for electrochemical reduction, MoO_3 and CaCl_2 reacts with each other and forms CaMoO_4 and volatile MoO_2Cl_2 gas as mentioned in section 2.3.1. Similarly, Erdoğan and Karakaya reported W loss by volatile WO_2Cl_2 gas formation during electrochemical reduction of WO_3 with a similar experimental route, and succeeded to produce W by the electrochemical reduction of CaWO_4 [24]. In the light of above findings, CaMoO_4 which forms when oxides of molybdenum come in contact with CaCl_2 was used as the starting powder in one of the sets of experiments [24]. A SEM image of the starting CaMoO_4 powder is shown in Figure 4.1. Similar to above mentioned study [24], the experiment was performed at 600°C in $\text{CaCl}_2\text{-NaCl}$ (50% CaCl_2 -50% NaCl) eutectic salt mixture under 2.8 V constant potential difference. Applied potential difference (2.8 V) was under the decomposition potentials of salts which were 3.3 V for CaCl_2 and 3.4 V for NaCl at this temperature. The XRD result and a SEM image of the sample after the experiment are given in Figure 4.2 and Figure 4.3, respectively. There was no Mo phase in the produced powder. The reason was considered to be the sintering of the pellet during the experiment at 600°C because the melting temperature of CaMoO_4 is 965°C [25]. When the pellet was sintered, CaMoO_4 , current collector and salt mixture contact might have become lost after the reduction at the bottom of the pellet was completed. The reduction probably started at the bottom of the pellet where it was in contact with the stainless steel spoon and slowed down as the reduction progressed to the inner parts. The presence of MoO_2 can be explained with reference to partial reduction of CaMoO_4 to MoO_2 and the reduction might have involved more than one stage.

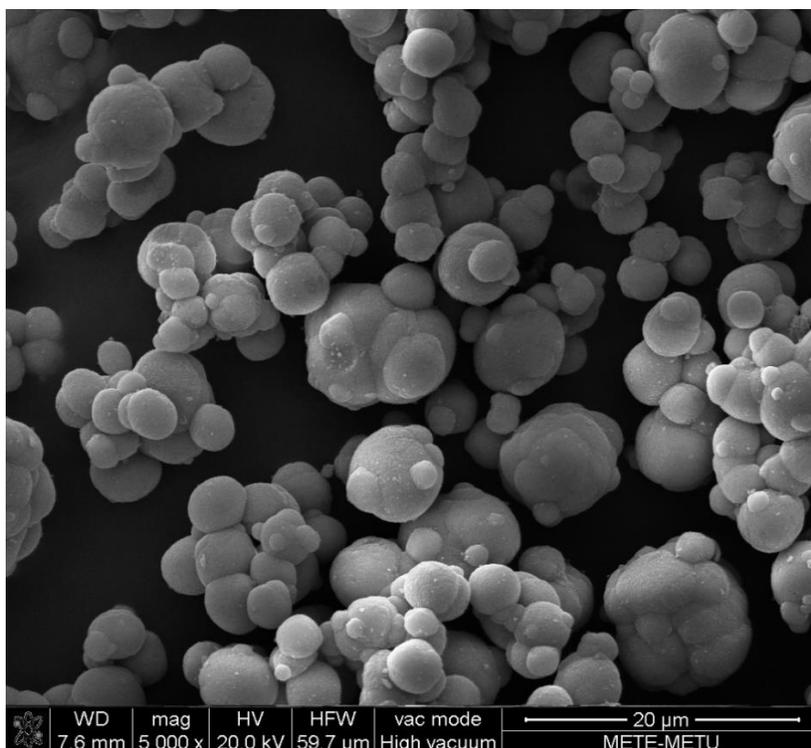


Figure 4.1. SEM image of CaMoO₄ powder

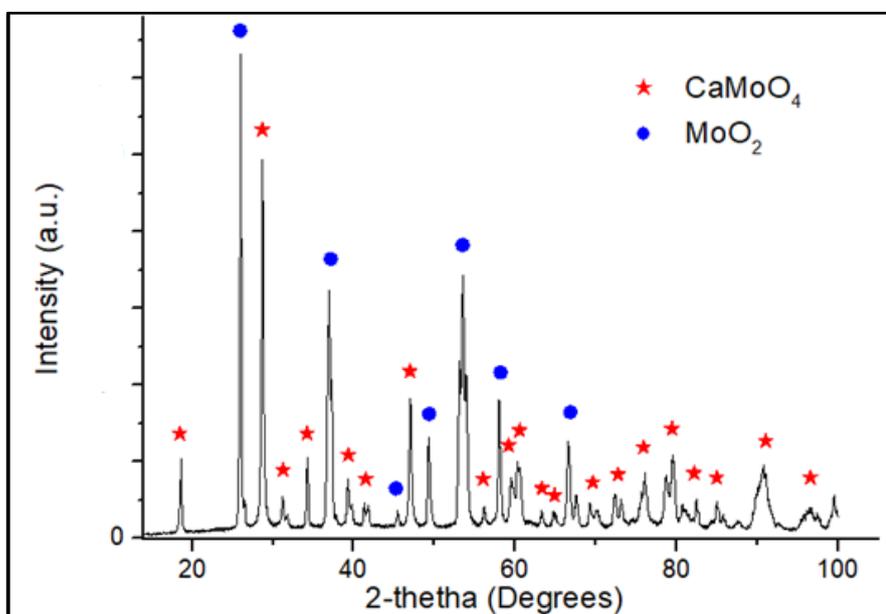


Figure 4.2. XRD result of the product from the experiment by CaMoO₄ starting powder at 600°C.

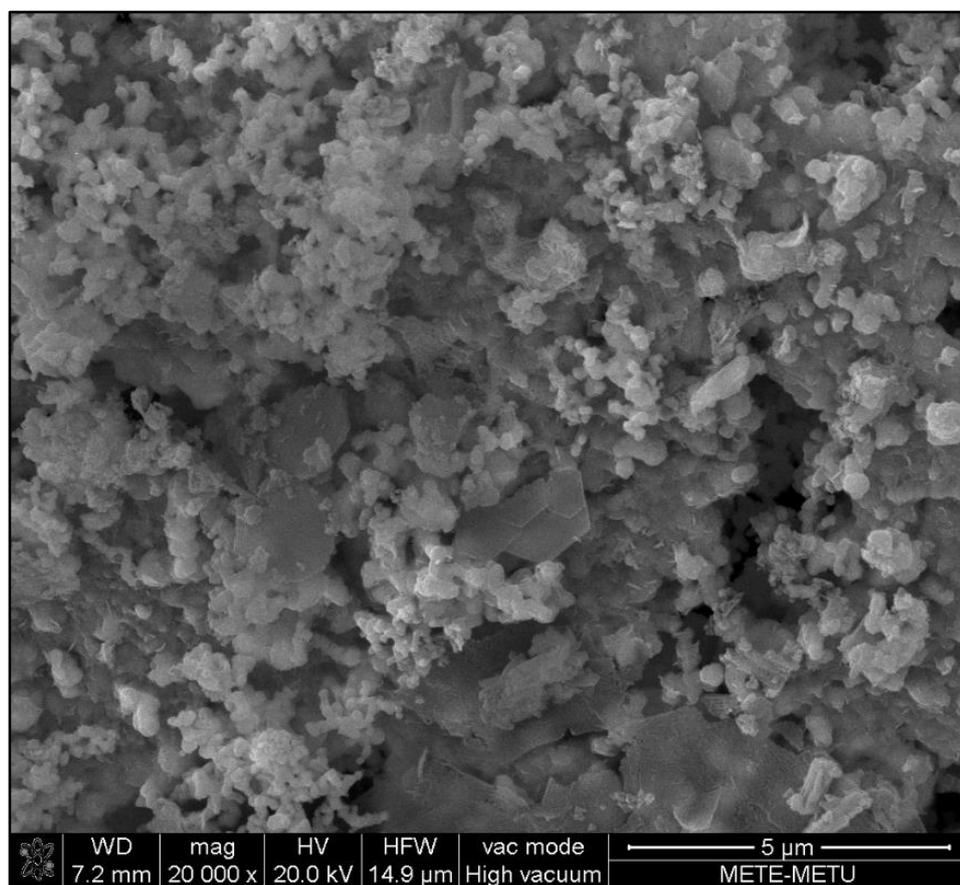


Figure 4.3. SEM image of the product from the experiment by CaMoO_4 starting powder at 600°C .

Gordo and Chen reported that the rate limiting step of the reaction during electrochemical reduction of solid oxide in molten salt was the diffusion of oxygen in the solid phase [20]. In the following experiment, temperature was increased up to 750°C to increase diffusion rate in the solid phase. As the temperature was increased, more CaCl_2 salt, which had higher oxide solubility compared to NaCl , could be used. Therefore, 70% CaCl_2 -30% NaCl salt mixture was used instead of eutectic salt mixture to improve reaction kinetics. The result of XRD analysis of the sample taken from spoon after the experiment is shown in Figure 4.4. Contrary to the result of the previous experiment, reduction was seen after this experiment; however, most of the produced

molybdenum reacted with carbon, which was eroded from graphite anode and carried by the electrolyte to the cathode, to form Mo_2C . A SEM image of the produced powder is given in Figure 4.5.

Less than 50% of the starting molybdenum in the form of CaMoO_4 pellet was recovered from the stainless steel spoon after the experiment as Mo and Mo_2C . As a result of this, it was decided to study the solubility of CaMoO_4 in the salt mixture. There was not any information about the solubility of CaMoO_4 in $\text{CaCl}_2\text{-NaCl}$ salt mixtures; therefore, further experiments were done for solubility to both contribute to literature and interpret the present results more clearly.

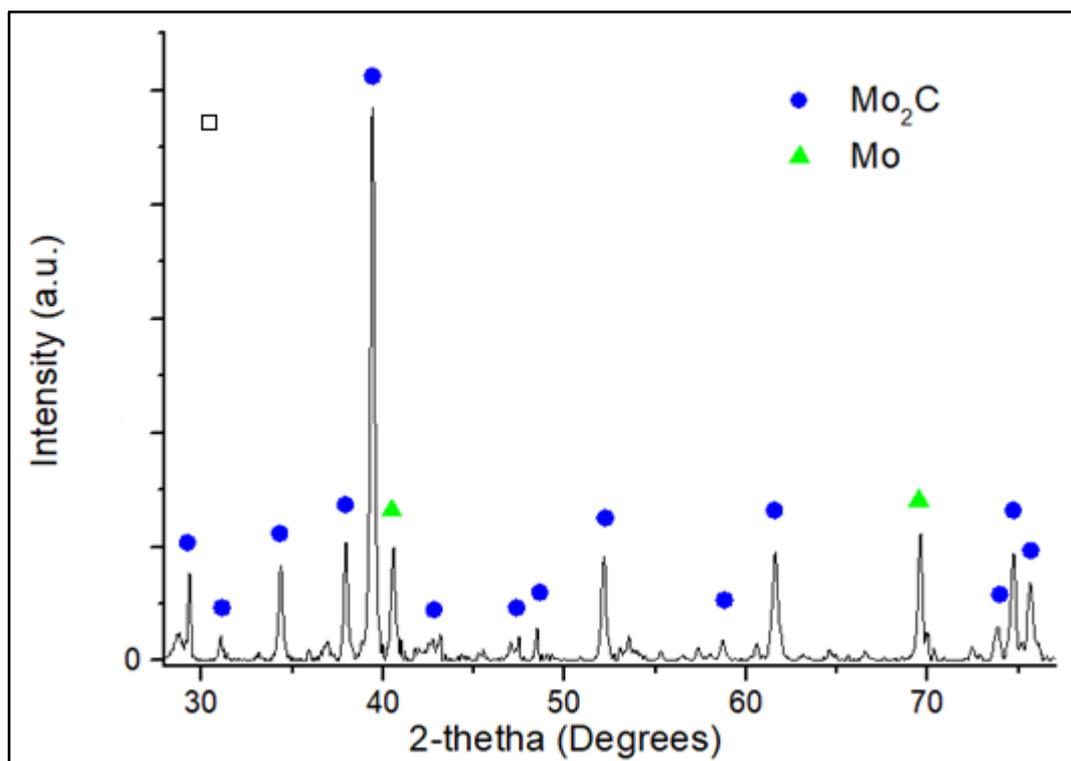


Figure 4.4. XRD result of the experiment done by CaMoO_4 starting powder and performed at 750°C . Undefined low intensity peaks belong to salt residual.

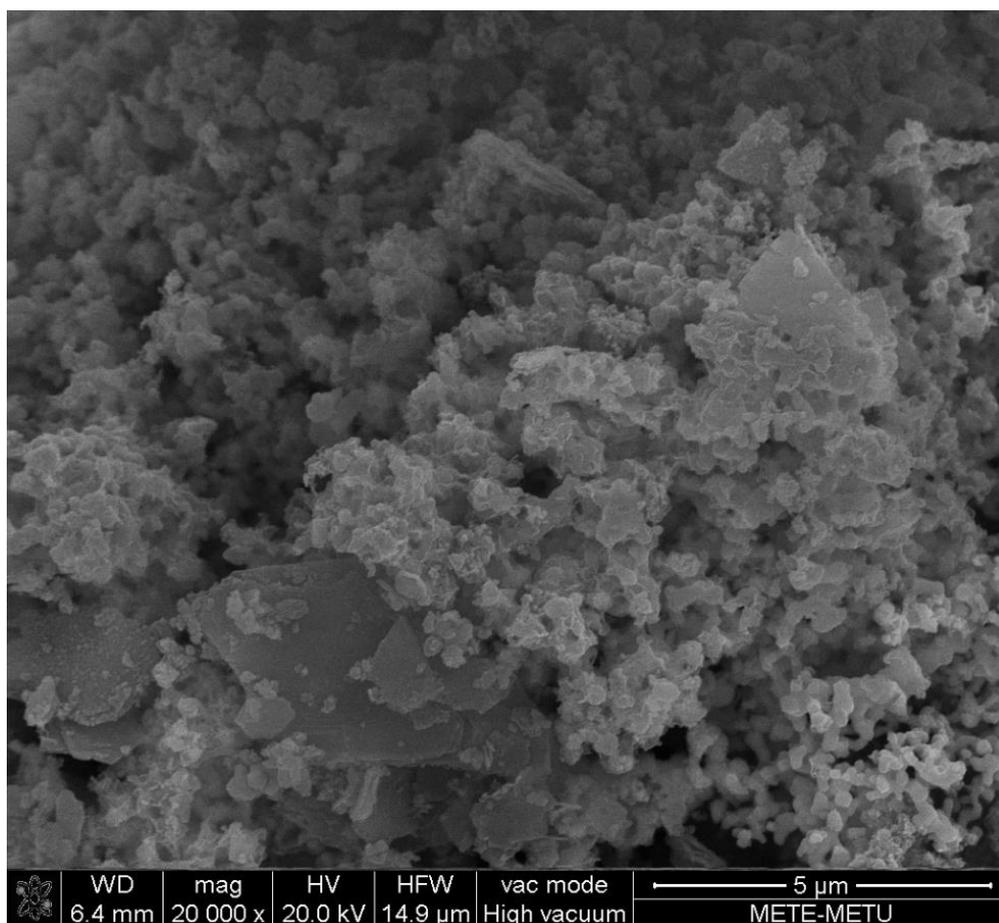


Figure 4.5. SEM image of the sample

4.2. Solubility of CaMoO_4 in CaCl_2 - NaCl Salt Mixture

At the beginning of solubility experiments, 2 grams of CaMoO_4 pellet was placed to the edge of a tungsten plate which was welded to a tungsten wire and extended out of the furnace by a Kanthal wire. It was submerged into 70% CaCl_2 -30% NaCl salt mixture at 750°C and waited for 12 hours. Salt samples were taken after 3 hours, 6 hours and 12 hours till the sample was taken out from the salt. The amount of salt collected from the system was 5.26 grams. After the sample was washed with distilled water to dissolve the salt and obtain the rest as a solid powder, the amount of final

solid powder was 0.21 gram. In order to determine the composition of the powder, XRF analysis was performed and its result is given in Table 4.1.

Table 4.1. Percentages of elements from XRF analysis.

<i>Element</i>	<i>Percentage (%)</i>		
	For 3 hours	For 6 hours	For 12 hours
<i>Mo</i>	62.7	63.8	67.3
<i>Ca</i>	37.3	36.2	32.7

XRF analysis of the very light element oxygen was not reliable for the machine used for analysis. Therefore, only the calculated percentages of Mo and Ca for 3 hours, 6 hours and 12 hours are given in Table 4.1 by excluding the oxygen. If the whole powder obtained at the end were CaMoO_4 , weight ratio for Ca/Mo would have been 0.42. However, the ratio given in Table 4.1 is 0.49 for the sample taken from experiment at the end of 12 hours. This result pointed out that there was another Ca based compound in the system in addition to CaMoO_4 . It was considered that this compound could be CaO which inevitably forms during the drying procedure of CaCl_2 . CaCl_2 salt is very hygroscopic. It is found to contain up to 6 moles of crystal water in nature (see phase diagram CaCl_2 and H_2O shown in Figure 4.6). This salt was subjected to drying before the experiment. However, it is inevitable to obtain oxide free CaCl_2 salt at high temperatures, because chemical bonds between CaCl_2 and H_2O cannot be completely broken during drying under argon flow. Any crystal water, left in connection with CaCl_2 will yield CaO formation at high temperatures.

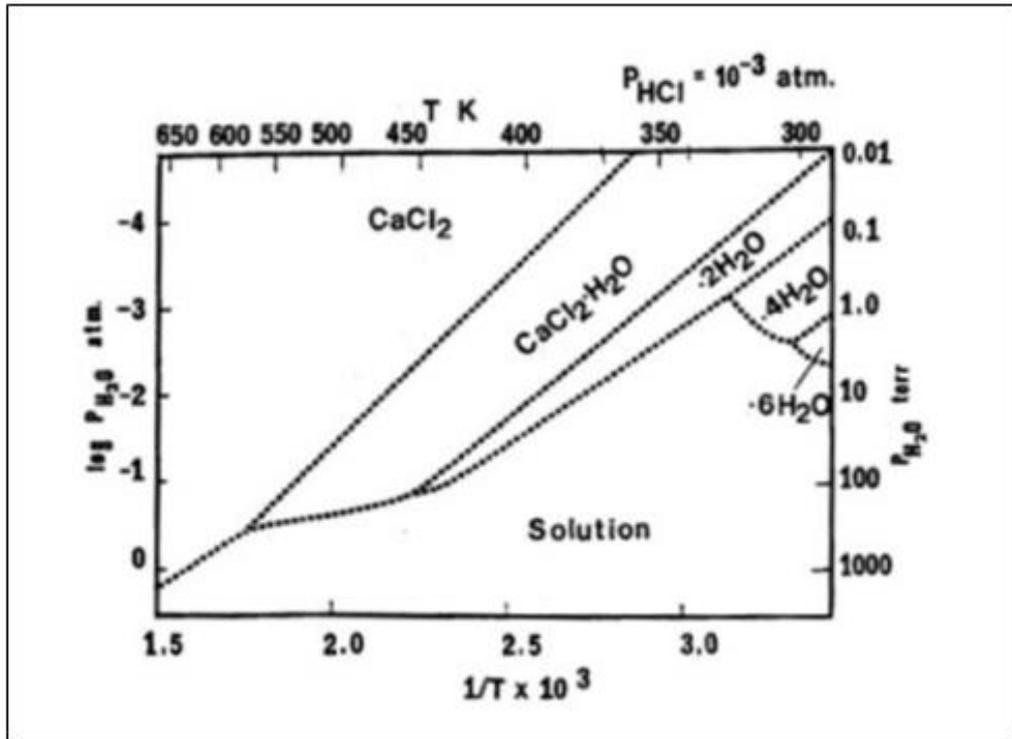


Figure 4.6. Phase diagram of CaCl₂ and H₂O [27].

The XRD pattern of the powder sample given in Figure 4.7 proved this hypothesis. CaO present in the powder reacted with H₂O to form Ca(OH)₂ while dissolving the salt in water.

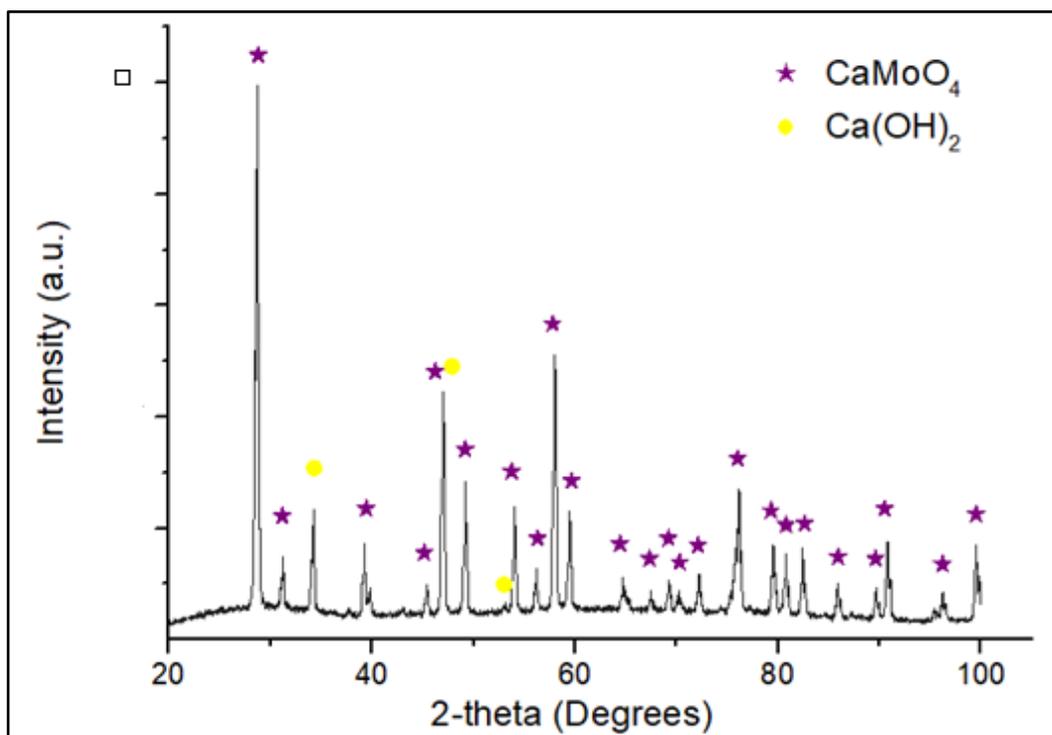


Figure 4.7. XRD result of solid powder collected from salt samples after the experiment done by CaMoO_4 starting powder and performed at 750°C for 12 hours to study solubility.

Therefore, 0.21 gram powder was composed of CaMoO_4 and Ca(OH)_2 and it was found that only 0.10 gram of this powder was CaMoO_4 by the help of the XRF analysis given in Table 4.1. Since this CaMoO_4 amount was obtained from 5.26 grams salt, solubility of CaMoO_4 in the salt mixture at 750°C was calculated as 1.9%.

In the electrochemical reduction experiments, 2 grams of CaMoO_4 pellets were used in 100 grams of salt mixture. Therefore, almost all of CaMoO_4 would be dissolved at 750°C after 12 hours. However, the XRD pattern of the sample at 750°C shown in Figure 4.4 showed that about half of the Mo from the beginning was obtained on the spoon probably because the current was immediately supplied as the electrodes were immersed into the salt mixture. Both dissolution process and electrochemical reduction might have taken place at the same time.

It can also be possible to collect dissolved Mo ion from the salt by electrolysis. However, the Mo powder obtained by this method would be in solid phase at this temperature. Since it would have been obtained from a liquid phase, the final product would have a dendritic structure which is not suitable for further metallurgical applications.

4.3. Electrochemical Reduction of MoS₂

It was seen that CaMoO₄ could not be used as a starting material to produce metallic Mo powder due to its solubility in CaCl₂-NaCl salt mixture. Therefore, another compound (MoS₂), which was also the most abundant Mo-containing mineral, was used as the starting material. An SEM image of the powder can be seen in the Figure 4.8. In 2007, Li and Wang reported that electrochemical reduction of MoS₂ to produce Mo powder in molten CaCl₂ salt was possible [26]. In this study [26], the pellet sintered at 300°C was reduced to Mo and S. Part of the S that was formed during the experiment reacted with carbon from graphite anode and formed CS₂. Electrochemical reduction process was performed at 800-900°C under argon gas for 1 to 20 hours.

In the present study, pellets were used without sintering unlike the above mentioned study [26]. In this study, MoS₂ pellet was fixed to a tungsten wire. This cathode assembly was dipped into the eutectic CaCl₂-NaCl salt mixture at 600°C and 2.8 V constant voltage difference was applied for 12 hours in the first experiment. XRD analysis of the sample taken after the experiment is given in Figure 4.9. As can be seen in Figure 4.9, almost no reduction was observed.

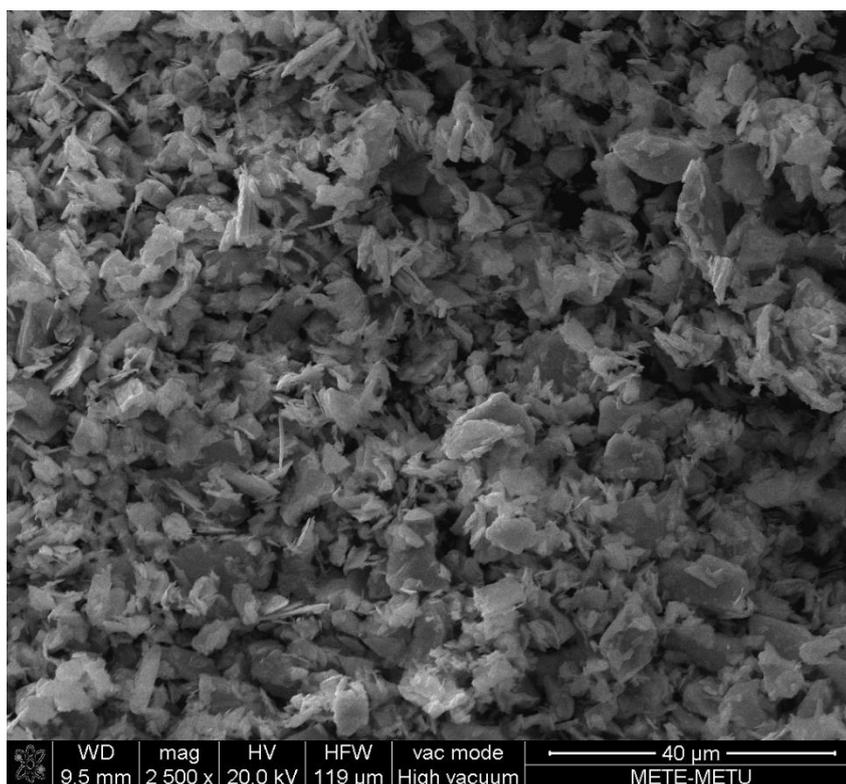


Figure 4.8. SEM image of MoS₂ powder.

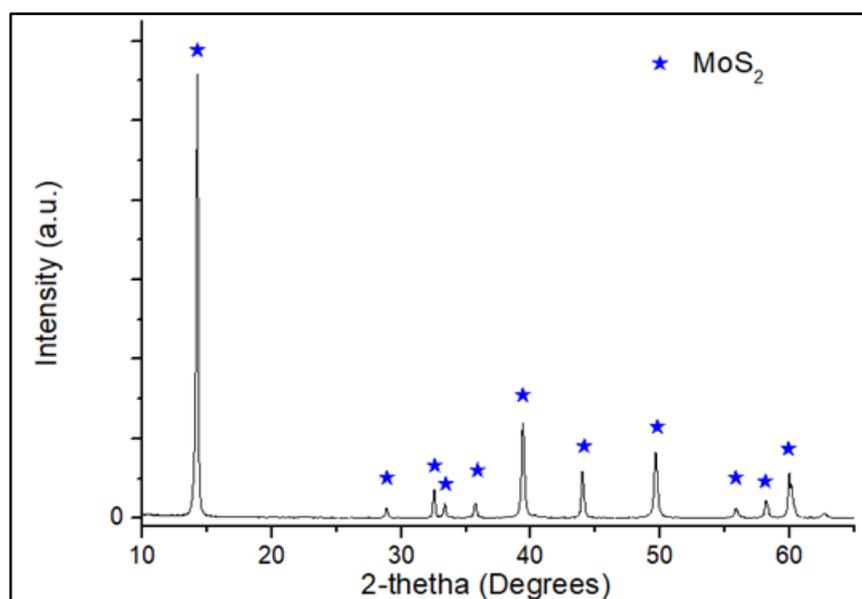


Figure 4.9. XRD result of the experiment done by MoS₂ starting powder and performed at 600°C.

In the next experiment, temperature was increased to 750°C and the composition of the salt mixture was readjusted as 70% CaCl₂-30% NaCl to enhance the reaction kinetics. Applied potential was again 2.8 V to examine the effect of temperature on reduction of MoS₂. The XRD pattern of the sample obtained after the experiment performed at 750°C for 10 hours is given in Figure 4.10.

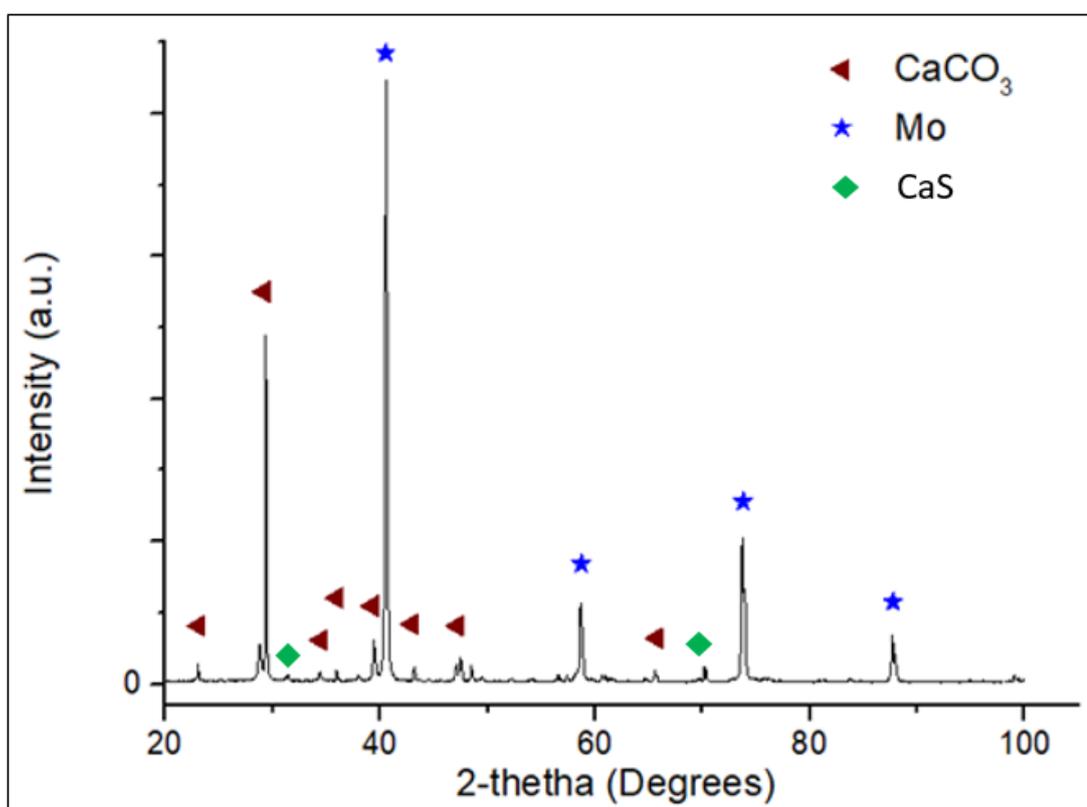
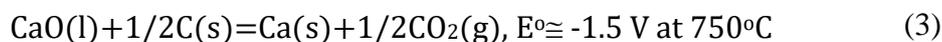


Figure 4.10. XRD result of the experiment done by MoS₂ starting powder and performed at 750°C

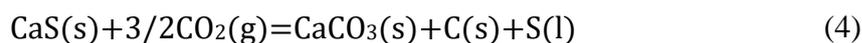
In Figure 4.10, it was seen that production of Mo at 750°C was successful together with CaCO₃ compound which is a usual by-product in electrochemical reduction processes of oxygen containing compounds [24]. CaCO₃ phase is formed by the reaction of CO₂ evolved at the anode and Ca and/or CaO present at the cathode after the completion of the experiments [24].

It is not possible to have such an oxidation reaction at the cathode. Therefore, the reaction took place when the electrolysis was completed and the current was turned off. Although the starting material in this experiment, MoS₂, did not contain any oxygen contrary to the above mentioned study [24], the evolution of CO₂ at the anode can still be explained with reference to high CaO solubility of CaCl₂ as mentioned before. Formation of CaO is almost inevitable during the drying process of CaCl₂ regardless of the attention paid, as can be seen in Figure 4.6. The applied potential difference of 2.8 V, was sufficiently high for the below reaction even after the voltage losses due to polarizations and resistances are considered:



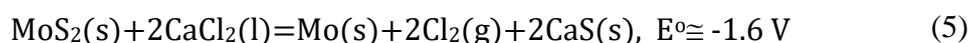
Therefore, another experiment was conducted under the same conditions. However, the reaction vessel was flushed with argon gas at the end of the experiment to take all the CO₂ out of the vessel before switching the current off. The XRD pattern of the cathode sample is given in Figure 4.11. As can be seen in this figure, the formation of CaCO₃ was inhibited.

This XRD pattern also revealed that the calcium compound present at the cathode and reacting with CO₂ was probably CaS. The equilibrium calculations [14] demonstrated that CaS and CO₂ react to form CaCO₃ according to the below reaction:

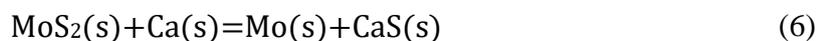


The above reaction becomes more favorable as the temperature decreased [30]. Therefore, the conditions were appropriate for the reaction when the current was turned off and the cathode was taken above the salt level to cool down in the previous experiment.

Based on the products of the electrochemical reduction experiment conducted at 750°C and chlorine evolution which was detected from the strong odor of this gas during the experiment, the below reaction was suggested:



It should be noted that the reaction given in Equation 3 was taking place simultaneously with Equation 5. Produced Ca metal could react with MoS₂ to reduce it according to:



However, the reactions given in Equation 3 and Equation 6, do not explain the chlorine gas evolution. Therefore, it is proposed that both mechanisms, Equation 5 alone and Equation 3 followed by Equation 6, were operative at the same time to produce the metallic Mo and the byproduct CaS.

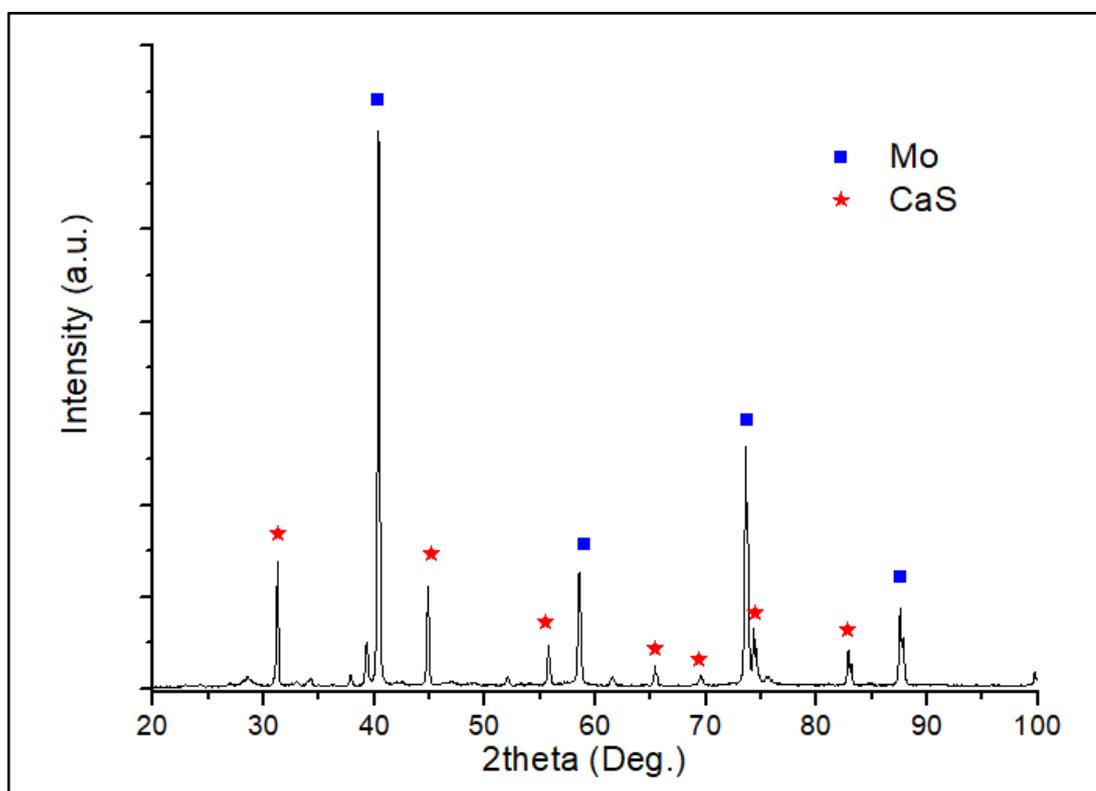


Figure 4.11. XRD result of the experiment done by MoS₂ starting powder and performed at 750°C while reaction vessel flushed with Argon gas at the end of the experiment.

In order to see the effect of increased temperature, another experiment was performed at 900°C. Increasing temperature was expected to help diffusion of sulfur in solid state

and improve reaction kinetics. Current vs. time graphs obtained in both electrochemical reduction experiments, at 750 and 900°C, are given in Figure 4.12. Both graphs possessed the general characteristics of electrochemical reduction experiments. The graphs started with a current peak because the pellet-salt-current collector interface was maximum at the beginning of the experiments. As the reaction proceeded, the current started to decrease because the solid-state diffusion path increased for S atoms. As can be seen in Figure 4.12, increasing the temperature increased the current and hence, decreased the time required for complete reduction. The XRD analysis of the sample produced at 900°C is given in Figure 4.13. Figure 4.13 proved that molybdenum was produced again with the by-product CaS. Some peaks with small intensities were considered to be originated from salt mixtures and not labeled.

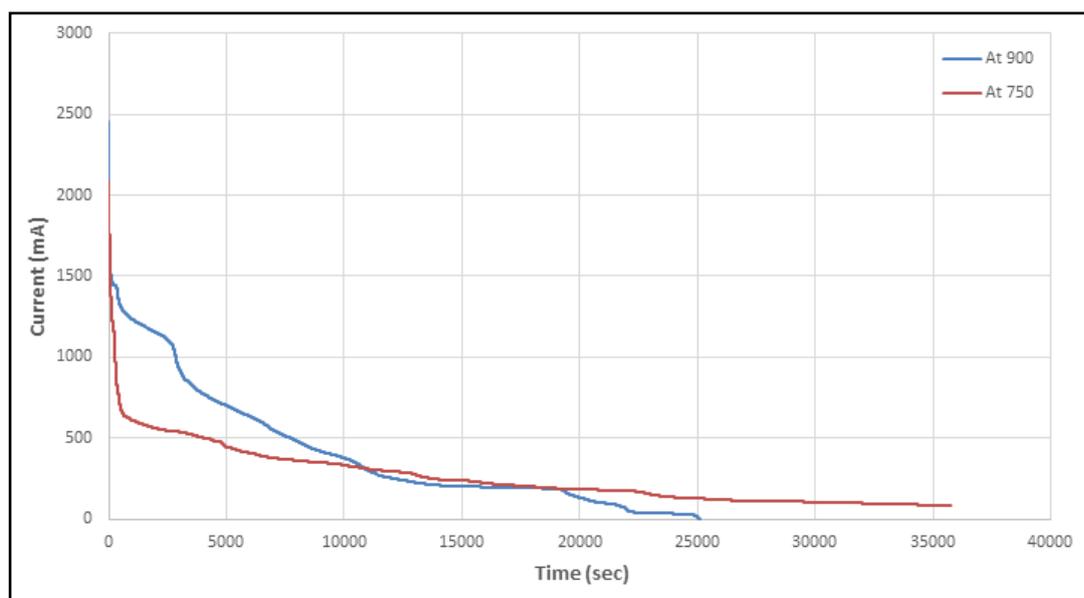


Figure 4.12. Current vs Time graph of the sample performed at 750°C and 900°C.

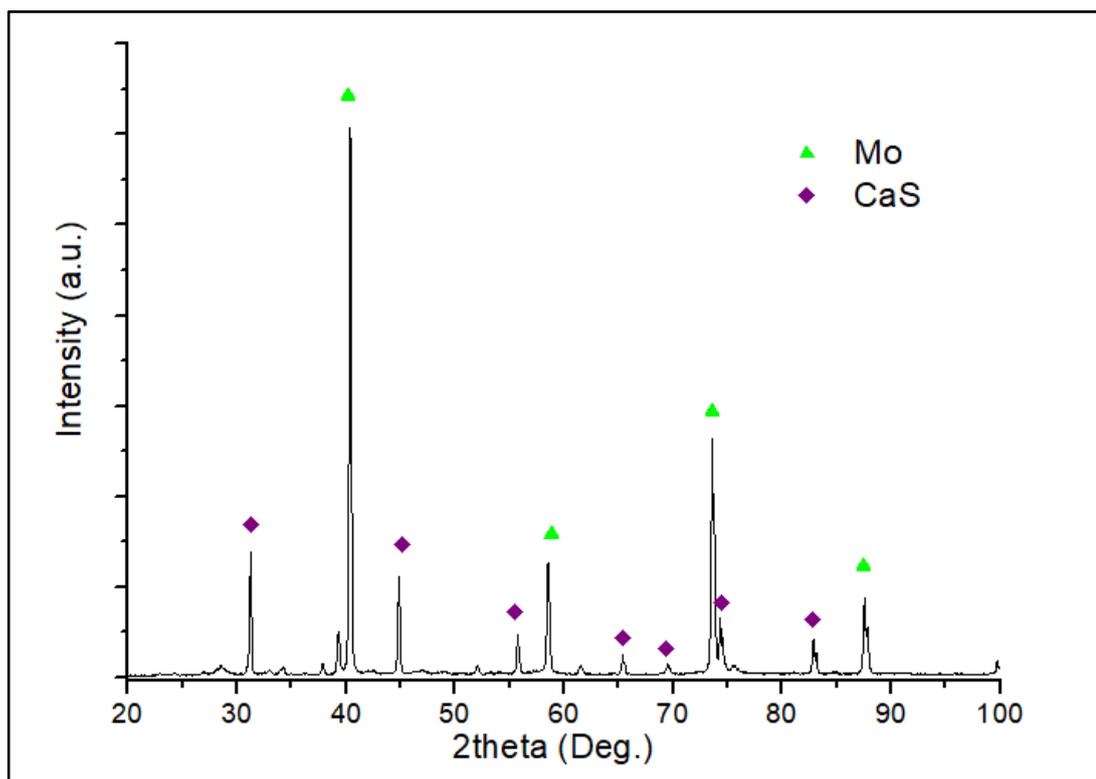


Figure 4.13. XRD result of the experiment done by MoS₂ starting powder and performed at 900°C while reaction vessel flushed with Argon gas at the end of the experiment.

The byproduct CaS can be removed by a dilute acid treatment in which molybdenum is sufficiently inert. Figure 4.14 and Figure 4.15 were obtained after exposing the products of the electrochemical reduction experiment to a 0.2 M HCl solution at room temperature for 15 minutes. As can be seen in these figures, both XRD and EDS results proved that CaS could be removed completely. An SEM image of the produced Mo powder is given in Figure 4.16.

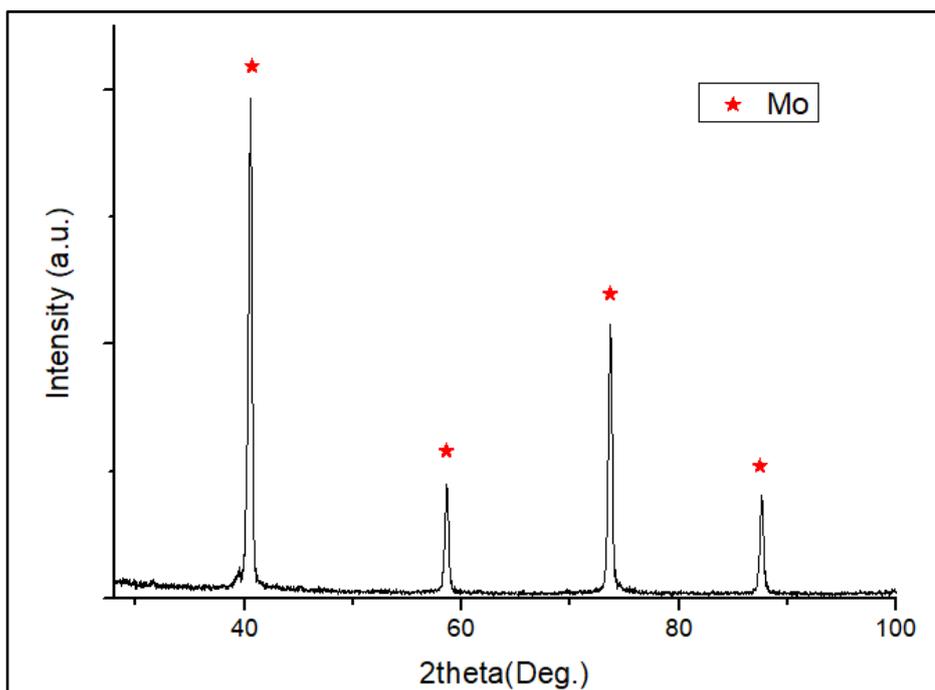


Figure 4.14. XRD pattern obtained after HCl solution treatment

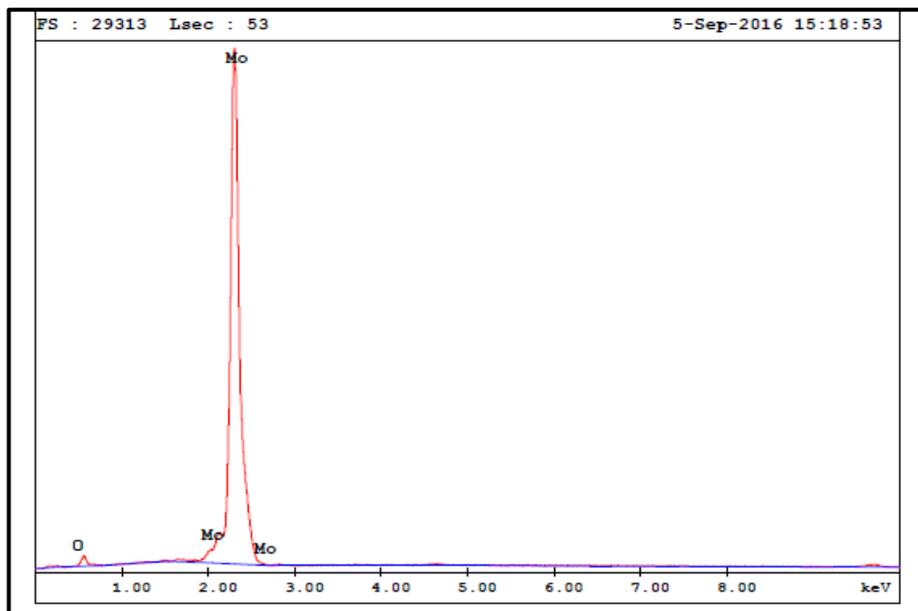


Figure 4.15. EDS analysis of sample taken after HCl solution treatment

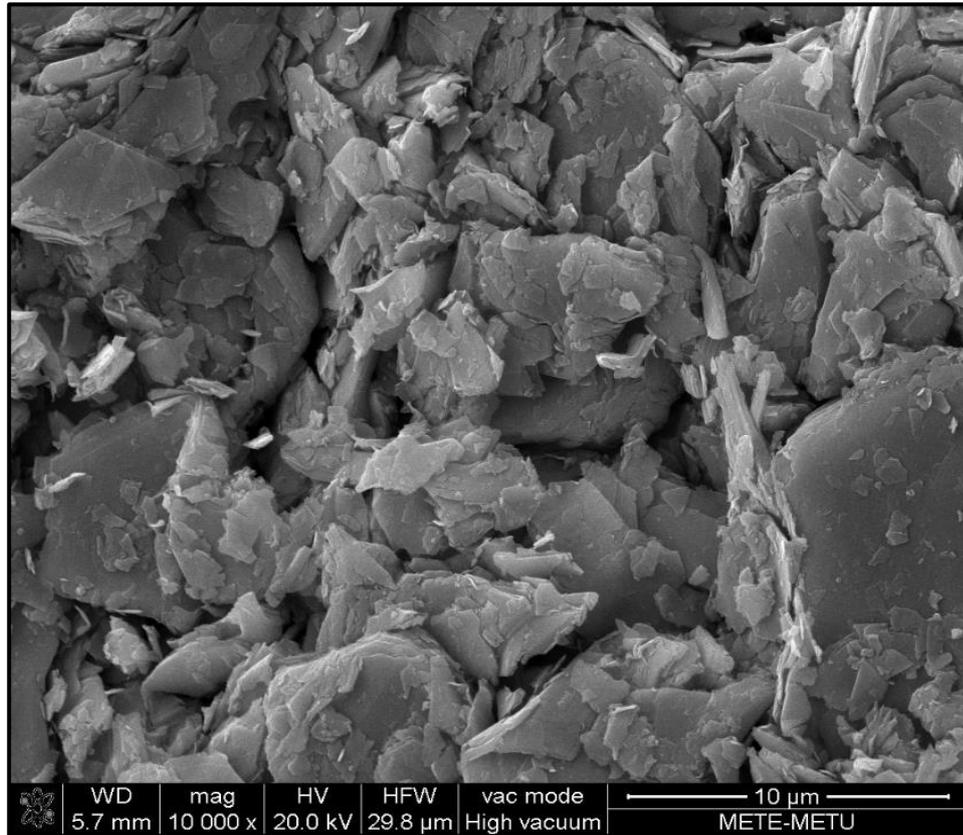


Figure 4.16. SEM image of the produced Mo powder.

4.4. Calculation of Electrical Energy Consumption

Theoretical charge for experiments can be calculated by Faraday's law of the electrolysis, which is shown in equation (7):

$$Q \times A \times CE = W \times z \times F \quad (7)$$

where Q is the charge in coulombs which is equal to current in amperes multiplied with time in seconds. A is the molecular weight of the MoS_2 , W is the amount of the reduction, z is the valance number, F is the Faraday constant (96500 coulombs) and CE is the current efficiency.

The accumulative electrical charge, Q , is present in equation (8) and total charge vs. time graph of the experiment performed at 900°C shown in Figure 4.17.

$$Q = \int_0^t I dt \quad (8)$$

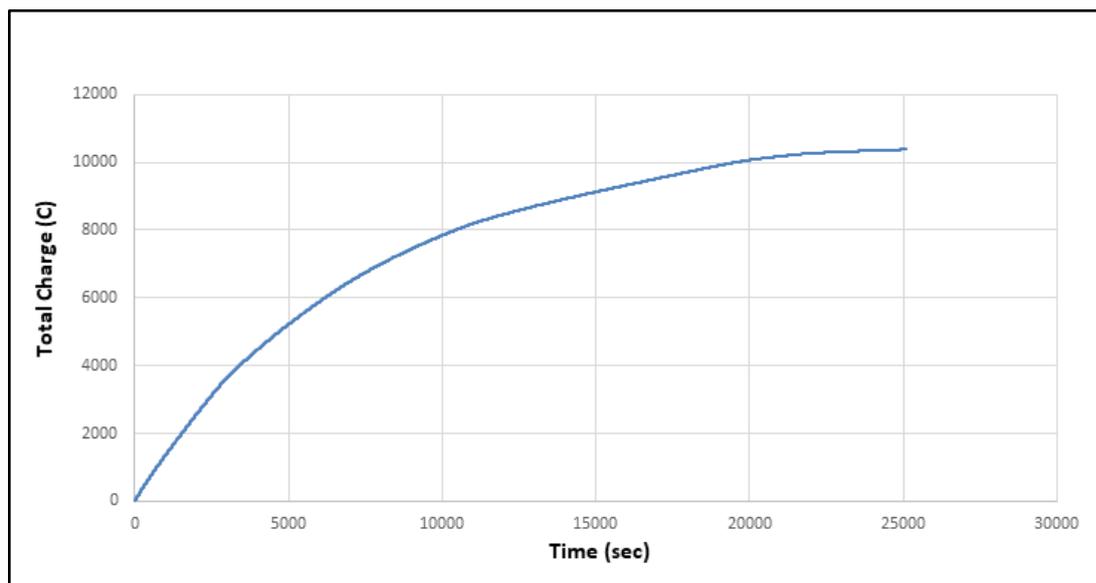


Figure 4.17. Total charge vs time graph of experiment performed at 900°C.

Reduction process during the experiment was complete at around 20000 seconds according to current vs. time and total charge vs. time graphs in Figure 4.12 and Figure 4.17, respectively. It is seen that nearly 10000 coulombs of electrical charge passed through the system until the reduction was complete. However, for complete reduction of 2 g of MoS_2 samples used during the experiments, theoretical charge requirement is calculated as 4824.25 coulombs from Equation 7. Therefore, the current efficiency of the reduction process to produce molybdenum was around 48%.

During the experiments, energy consumption (ε) as a function of time can be calculated according to Equation 9. This is also equal to multiplication of charge Q with the applied potential.

$$\varepsilon = \int_0^t I V dt \quad (9)$$

Electrical energy per kilogram of molybdenum production can be calculated by the Equation 10.

$$E \text{ (per kg Mo)} = \frac{1000}{m} * \varepsilon \quad (10)$$

where m the is amount of molybdenum collected after each experiment in grams. Theoretically, produced molybdenum from 2 g of MoS₂ powder is 1.2 g and the charge is 4824.25 C. Therefore, electrical energy required per kg of molybdenum production is 3.127 kWhr/kg, theoretically. However, during the process 10000 C was passed through the system for complete reduction and current efficiency was around 48%. As a result of this, electrical energy required per kg of molybdenum production at 900°C is calculated as 6.5 kWhr/kg, approximately.

This electrical energy consumption is even comparable to the electrical energy requirement of the hydrogen production process by electrolysis, which is used to reduce molybdenum oxides in the current molybdenum production technique. Therefore, it is clear that the electrochemical reduction process has the potential to be much more economical than the current production method.

CHAPTER 5

CONCLUSION

Refractory Mo metal powder production by electrochemical reduction of CaMoO_4 and MoS_2 powder was studied. All experiments were implemented under constant voltage of 2.8 V and argon gas in CaCl_2 - NaCl molten salt solutions.

Reduction of CaMoO_4 powder was not feasible because experiments showed that CaMoO_4 was soluble in CaCl_2 - NaCl salt mixture. In order to understand the solubility of the CaMoO_4 , salt mixture was heated up to 750°C and samples were taken after 3, 6 and 12 hours from the salt. XRF and XRD results combined with calculations showed that CaMoO_4 had about 1.9% solubility in eutectic CaCl_2 - NaCl solution.

Reduction of MoS_2 powder was successfully achieved in molten CaCl_2 - NaCl (70% mole-30% mole) salt mixture under argon gas at 750 and 900°C . XRD and EDS results proved the formation of Mo metal powder by electrochemical reduction together with the byproduct CaS . CaS could be removed completely by a dilute acid treatment at room temperature. Electrical energy required per kg of molybdenum production at 900°C was determined as around 6.5 kWh/kg.

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