Extraction of Mn and Cr from slags by molten salt electrolysis

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Abstract: There are many kinds of elements, especially heavy metallic elements, present in the industrial slags. These elements bring big environmental problems if they are directly used in land filling. And the recovery of these elements can also have benefits for the resource conservation. This paper reports the use of electrochemical method to extract the metal elements from both industrial slag and pure oxide. The mixture of NaCl-KCl was used as the electrolyte for this process. Some proposals are also mentioned for the further work.

Key words: Molten salts, Electrolysis, Slag, Cr, Mn.
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1. INTRODUCTION

Slag has a very important role in extraction of metals from ores. It separates the unwanted composition from the desired metal. Slag usually contains silicon dioxides and several kinds of metal oxides. The impurity removal is good for the process but the retention of the elements in the slag, not only add the waste of resources but also brings environmental problems. In this thesis work, the molten salt electrolysis is used to extract Cr and Mn.

2. BACKGROUND

Molten salts electrochemistry is a science which studies the chemistry changes while the DC power is applied to the molten salts or the current changes during the chemistry changes occur in the molten salts. So that we can say molten salts electrochemistry was born from molten salts electrolysis.

Molten salts electrolysis has a young history. In 1807, the English chemist H. Davy firstly recovered Na from NaOH. This is the first use of molten salts electrolysis to get metal value. Since then, the door of molten salts electrochemistry opened in front of all the chemists. In 1808, he performed electrolysis of KOH and got Potassium. Then the electrolysis of CaO and HgO mixture gave him Calcium amalgam, Barium amalgam from BaSO₄, and Magnesium amalgam from MgO. And in 1818, he got a little Lithium from Li₂CO₃. At the end of 19th century came the most valuable discovery, C. M. Hall from USA and P. L. T. Heroult from France got Aluminium from electrolysis of Cryolite - Alumina. Until today, this is still the most widely used method for industrial production of aluminium.

Theoretically, all the active metals or values can be made by electrolysis of molten salts, but due to molecular structure, conductivity while melted, process temperature and some economic consideration, only for some of the metals this method is used as the industrial production method. But for some metals, especially the ones whose deposition potential is negative, they cannot be electrolyzed in water solution because hydrogen evolution happens before reduction of the metal. The Table 1 shows the merit and drawback of molten salts electrolysis compared with electrolysis from water solution.

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Have wide voltage range</td>
<td>1. High temperature and high energy</td>
</tr>
<tr>
<td>2. High ion conductivity</td>
<td>2. High vapor pressure</td>
</tr>
<tr>
<td>3. High diffusion coefficient</td>
<td>3. High causticity</td>
</tr>
<tr>
<td>4. Low viscosity</td>
<td>4. Low current efficiency</td>
</tr>
<tr>
<td>5. High solubility for some salts</td>
<td>5. Salts will solidify if cut the current</td>
</tr>
<tr>
<td>6. High current and more product</td>
<td></td>
</tr>
<tr>
<td>7. Low over-voltage</td>
<td></td>
</tr>
<tr>
<td>8. High purity for some metals</td>
<td></td>
</tr>
</tbody>
</table>
2.1 Molten salts
Molten salts are much more complicate then the water solution, the study of the structure of molten salts can help us know more about the characters and give us a suitable explanation of the electrode process.

2.1.1 Structure of molten salts
The first one who proposed the concept of the molten salt is Farady in 1833. He indicated that there are positive and negative ions in the molten salts. Then during the recent years, many researchers built models for the structure of molten salts, such as the Quasi – Lattice model by Stillinger, Hole model by Bockris and Richards, Significant structure by Eyring and Liquid free volume model by Cohen and Turnbull. Since the computers are widely used in the research, people can easily built models by using the software. There are two computer methods used to build the models, Monte Carlo method (MC) and Molecular dynamics method (MD). MC method is based on the probability and statistics while MD method follows the Newton's equation of motion and both these two method are “hard core and soft shield” models. 

From the study of the molten salts structure, people found some common properties such as 1) The volume of the salts will decrease after melting; 2) The conductivity is higher in the molten salts for some elements; 3) The ion arrangement in molten salt is short-range ordered; and 4) The coordination number of the salts will decrease after melt and so on. These models can help us understand better about the molten salts, but models are only simulations of the system. The real salts are more complicate so maybe several models should be used together or these models can just point out the some trend of the process.

2.1.2 Conductivity of molten salts
In the real production of the metal using electrolysis, if current density and temperature are fixed, then the distance between anode and cathode depends on the conductivity of the electrolyte. So the study of conductivity of molten salts is necessary.

Similarly as water solution, molten salts also have conductivity and mole conductivity. Normally, the conductivity may have suddenly increased during the phase change of molten salts from solid to liquid. But while all the salts change into liquid phase, the conductivity will grow with the temperature linearly. And the conductivity of liquid phase is higher than solid phase. Special for AlCl\(_3\), when the temperature gets close to the melting point, the conductivity grows rapidly. But after it changes to liquid, the conductivity falls down to nearly zero then starts to grow with the temperature again. This phenomenon shows that liquid AlCl\(_3\) is no longer in ionic form but has a molecule structure.

The conductivity of molten salts depends on several parameters. Normally, the conductivity of molten salts increases with the temperature which can be show with the function below:

\[
\lambda = \lambda_0 \exp \left(-\frac{E_A}{RT}\right)
\]

\[
K = K_0 \exp \left(-\frac{E_K}{RT}\right)
\]

\(E_A\) and \(E_K\) are active energy of mole conductivity and conductivity which is the lowest kinetic energy of the ion to migrate from original position to a new one. Then for the relations between conductivity and viscosity of molten salts, it can be written in Arrhenius index:
\[ \lambda = A \exp \left( \frac{-W_\lambda}{RT} \right) \]
\[ \eta = B \exp \left( \frac{-W_\eta}{RT} \right) \]

Combine these two equations then we can get
\[ \lambda^n \eta = A^n B \exp \left( \frac{-nW_\lambda - W_\eta}{RT} \right) \]

So while the active energy of conductivity increases the active energy of viscosity decreases. As mentioned before, the mutation points are always corresponding to the conductive change point. So we can draw the diagram of the phase with temperature and conductivity.

### 2.2 Thermodynamic
#### 2.2.1 Phase diagram of molten salts
Phase balance and phase diagram is so important for study the thermodynamic properties of the molten salts, it shows the equilibrium system more intuitively. In real production, phase diagram is always used for chosen electrolytes in molten salts electrolysis or plating, in molten salts cells and reactor heat transfer medium. Although the technique of determination is more accurate and new equipment and software are used to make the results more reliable, there are too much details need to be considered. And the subject of the study of this phase diagram is called Computer Coupling of Thermochemistry and Phase Diagrams (CALPHAD) \(^4\). From the phase diagram, we can get the thermodynamic data of a system or we can plot the phase diagram with the data we get from the experiments.

#### 2.2.2 Thermodynamic model
There are many models developed to predict the thermodynamic properties of electrolyte solutions, including Debye-Hückel model which is the first model; Fowler and Guggenheim modified this model for mixed solvents; Bromley model which introduced a new parameter \( B_{MX} \) of ionic strength function; Meissner’s graphical method; Chen et al. NRTL theory; until 1990s Lin et al. proposed a TCPC model with the attribution of short-range ion-solvent molecule interaction to the solvation effect. \(^5\)
And with the computer technology used in the development, many models have been put forward. Ge Xinlei et al. modified the original TCPC model by Lin et al. After modification, the model equations are \(^6\)

\[ \ln \gamma_{\pm} = -|Z_+Z_-|A_\phi \left[ \frac{l_1^{1/2}}{1 + b l_1^{1/2}} + \frac{2}{b} \ln \left( 1 + b l_1^{1/2} \right) \right] + \frac{S}{T} \left( \frac{l_2^{2n}}{v_+ + v_-} \right) \]
\[ \phi = 1 - |Z_+Z_-|A_\phi \frac{l_1^{1/2}}{1 + b l_1^{1/2}} + \frac{S}{T(v_+ + v_-)} \frac{2n}{2n + 1} l_2^{2n} \]

Here \( b, S \) and \( n \) are adjustable parameters. The \( b \) is called “approaching parameter”, which is dependent on the closest-distance of approach between ions. \( S \) is defined as the “solvation parameter” that represents the solvation effect between ions \( i \) and the solvent molecules. And \( n \) can be called “distance parameter”, which is related with the distance between ion and solvent molecule.
2.2.3 Molten salt reaction
In molten salt electrolysis or electroplating or molten salt batteries, the essence is the chemical or electrochemical reactions in the molten salts or on the other phase contact surface. So the molten salts can be seen as high-temperature ionized solvents as water for aqueous solution. But these reactions are different with that in aqueous solutions, such as the reaction speed is faster due to the high temperature of molten salts, and some reactions which are irreversible at room temperature, can follow the law of chemical equilibrium in the molten salts in another words, they can happen in molten salt due to the increasing of the reaction temperature. For electrochemical reactions, molten salts have higher conductivity and ion migration rate, which can speed up the reaction and lower down the energy lost.

But molten salts are mixture of several salts normally not like just single solvent for aqueous and non-aqueous solutions. So people use a common ion \( O^{2-} \) to study the molten salts reactions. And \( E - p^{O2-} \) diagram is widely used to predict the possibility of selective dissolution of \( MO_x \) (M for metals) in alkali metal chloride.

2.3 Electrodes
2.3.1 Electrodes materials
Since molten salts electrolysis is processed at high temperature in high corrosive medium, there are strict requirement for the electrodes. Materials used as electrodes need to have good electrical conductivity, should be able to work under high temperature, easy to process and cheap. Suitable materials include some metals, carbon materials and ceramics. They each have their characteristics and can be used in different production processes.

We can simply classify them by the function of the electrode. For cathode, where metallic values and alloys are deposited, so it must have good chemical resistance to the products, for example the electrode cannot react with the products or dissolved in to the salts phase. And good wettability is also needed to increase the productivity and save the energy. Carbon materials have good high-temperature resistance, corrosion resistance and conductivity, and also this kind of materials is much cheaper than the others. But the wettability is not as good as others, for example in aluminum manufacture. Another kind of materials suitable to be used as cathode is ceramic. This kind of ceramic is so called refractory hard materials, including boride, carbide, nitride and silicide of some sub-group elements. At the anode, there is always some gas (\( O_2 \), \( CO_2 \), \( Cl_2 \), \( F_2 \), \( CF_4 \)) released. So the materials for the anode should have high oxidation resistance. In this case in addition to carbon materials and ceramics some metals can also be used as anode. But the metal should not contaminate with the product.

2.3.2 Electrode process
As other reaction or process, electrochemistry also has directions. It can expressed as chemical reaction reversible and thermodynamic reversible. For chemical reaction reversible, it can be seen from some cells such as \( Ag | AgCl | (Cl_2) C \). And if the current for a chemical reversible reaction is enough low, then this reaction can be recognized as thermodynamic reversible. But for a real reaction, it is always not in the equilibrium position; even people don’t want it to be reversible because we want to produce at a fast speed.

The electrode process between electrodes and medium is a special heterogeneous redox reaction in which electrons participated. Only electrons can pass though in electrodes, so ions will get or los
electrons at the surface of the electrodes. So that the reaction speed is depend on not only the surface area and properties of the electrodes, but also the mass transfer in liquid phase which means the supplement of the reactions and the evacuation of the products. And the electrode potential has the significant effect. [7]

The equilibrium potential equation export from the dynamics is similar to the Nerster equation

$$\varphi_e = \varphi^0 + \frac{RT}{nF} \ln \frac{c_D}{c_R}$$

only concentration instead of the activity. When electrode voltage is high, the electrodes reaction is under the strong polarization and over-voltage is proportional to the logarithm of current density for the cathode process. This is first found by Tafel in 1905, and the equation is

$$\varphi = a + blg_i.$$ If $\eta < \frac{10}{n} mV$, the electrode reaction is called under the week polarization. When electrode potential increasing, the current density will grow exponentially in high speed with the final data nearly to the limiting diffusion current, then the concentration difference will have apparent effect to the electrode potential. And this diffusion current is so called critical current. During the molten salts electrolysis, some reactions happened on the surface of the electrodes but with the characteristic of chemical reaction, which also follow the Tafel equation.

### 2.4 Extraction process

The electrochemical method for extraction normally has two steps: first, dissolve the slags or ores which have the metal elements we want into molten salts at a suitable temperature; then electrolyses the salts phase to recover the metal we want as cathode deposits. The flow chart is shown below. [6]

**Fig 1. Flow chart for extraction process**

#### 2.4.1 Results from Pre-study

Ge Xin’lei used this process to recovery Cr, Fe from EAF slags and chromite ore. The order of oxides dissolved in the molten salts from his study is ‘CaO>MnO>FeO>MgO/Cr2O3’, the more rearward the oxide the easier it will be recovered. The optimized process parameters from the study were (a)
temperature of 950°C (b) flux/slag (weight ratio) at 1.5 or 2, (c) holding time of 8h and (d) flux content (mole ratio) of 30%. [6]

2.4.2 Potential for electrolysis
The main reaction for the electrolysis could be

\[
MO_x + AlCl_3 \rightarrow MCl_x + Al_2O_3
\]

\[
MCl_x \rightleftharpoons M + Cl_2(g)
\]

\(M\) represents the metals.
The \(Cl_2\) gas produced at anode can also react with oxides to dissolve more slag or ore into the salt phase.

\[
MO_x + Cl_2 \rightarrow MCl_x + O^{2-}
\]

For this method, a constant voltage is needed. And the potential for electrolysis can be calculated using Nernst equation.

\[
E = E^0 - \frac{kT}{n} \ln Q
\]

\(E^0\) is the standard potential and can be instead by \(\Delta G^0\).
\(n\) is the number of the charge.
\(Q\) is defined as the reaction quotient.
During the electrolysis, there will be a polarization so the over potential is needed.

2.4.3 Electrolysis time
Electrolysis time is an important parameter to control the procedure. Here for estimate the electrolysis time, Faraday’s laws of electrolysis are used. The equation is

\[
n = \left(\frac{Q}{F}\right) \left(\frac{1}{z}\right)
\]

\(n\) is the amount of substance \(n = m/M\)
\(Q\) is the total electric charge \(Q = It\)
\(F\) is Faraday constant
\(z\) is the valency number of ions
But the time for the electrolysis will also be affected by composition of the sample especially for the industrial slag. If the time is too short the yield will be low, but longer time may also bring the impurity of the product.

3. EXPERIMENT METHOD

3.1 Equipment and salts system
3.1.1 Cr electrolysis
Figure 3.1 and 3.2 are the equipments for the experiment of big scale. The heating elements are around a stainless steel container. An alumina crucible (OD 120mm, height 300mm, thickness 5mm) was used to load the salts. The salts NaCl (99%), KCl (99%) and slags were dried. The argon gas is supplied by AGA Gas AB in Sweden (99.999%). Both anode and cathode are graphite. The size of the electrodes is diameter 8mm and length 600mm. HP Hewlett 6673A DC power suppler was used to give a constant
voltage DC. The ratio of the molten salts is based on Ge Xinlei’s report and listed in the Table 2 with flux/slag at 1.5 and flux content of 30%. The slag sample is after oxygen blowing from Uddeholm Tooling AB. And the main compositions of slag are listed in Table 3.

Table 2. Molten salts composition for big scale experiment

<table>
<thead>
<tr>
<th>Name</th>
<th>NaCl</th>
<th>KCl</th>
<th>AlCl₃</th>
<th>Slag</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (g)</td>
<td>115.7</td>
<td>147.5</td>
<td>157.9</td>
<td>78.9</td>
<td>500</td>
</tr>
</tbody>
</table>

Table 3. Composition of the slag for tooling steel

<table>
<thead>
<tr>
<th>SiO₂</th>
<th>CaO</th>
<th>Cr₂O₃</th>
<th>FeO</th>
<th>MnO</th>
<th>Al₂O₃</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.9</td>
<td>28.7</td>
<td>18.5</td>
<td>4.7</td>
<td>1.7</td>
<td>7</td>
<td>16.6</td>
</tr>
</tbody>
</table>

Fig 2. The electrolysis equipments including furnace, container, electrodes, power supplier and gas system.

Fig 3. The schematic for Cr electrolysis equipment.
3.1.2 Mn electrolysis

The equipments for Mn experiments are in lab scale. The figure 4 below is the schematic.

![Fig 4. The schematic for the Mn electrolysis equipment.](image)

A small alumina crucible (OD 38mm, height 58mm, thickness 2mm) with lid was used to hold the salts. Electrodes were still graphite (diameter 6mm, length 400mm). This Mn electrolysis is just to test and verify that Mn can also use this method to recover. So we use the pure MnO for the experiment. The amount of the chemicals is listed in the Table 4 with the same flux content and flux/MnO ratio. Argon without moisture was supplied to protect the system.

### Table 4. Molten salts composition for lab scale experiment

<table>
<thead>
<tr>
<th>Name</th>
<th>NaCl</th>
<th>KCl</th>
<th>AlCl₃</th>
<th>MnO</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (g)</td>
<td>6.5</td>
<td>8.5</td>
<td>6</td>
<td>4</td>
<td>25</td>
</tr>
</tbody>
</table>

3.2 Experiment process

3.2.1 Cr recovery

Firstly, the salts NaCl, KCl and slags powder were mixed together and put into oven at 110°C to remove the moisture. After that, AlCl₃ was put firstly to the bottom of the alumina crucible then the dried salts mixture on top. The stainless steel container was sealed and vacuumed before filling in argon gas. Before come into the container, the argon gas was flowed pass silica gel to remove the moisture. The exhaust was passing through gas washing bottles with oversaturated solution of calcium oxide to absorb the excess Cl₂ gas. The temperature was set to 850°C. At this temperature the electrolysis potential is around 2 volt but due to the over potential, the electrolysis voltage we use was 3.5 volt. It needs almost 8 hours to heat the system to aim temperature. Then temperature was balanced and the molten salts were dissociation for another 8 hours. During these steps mentioned above, the graphite electrodes were put 3cm above the salts bath. Then they were push down 1cm above the bottom of the crucible. The electrolysis time was calculated use the Faraday’s equation and the current was read from galvanometer. It took almost 8 hours for the electrolysis. After electrolysis electrodes were pulled out of the salts bath.
and the system was cooling down to the room temperature. Then electrodes were taking out and the salts that stick on the electrodes were washed away using ethanol. And the samples should be analyzed by X-Ray Diffraction, and Scanning Electron Microscope (SEM) equipped with Energy-Dispersive X-ray Spectrometry analysis (EDS).

3.2.2 Mn recovery
The steps for Mn recovery are similar to the Cr recovery. Firstly, prepare for the salts mixture then do the electrolysis. Because the raw material is different, this experiment we use 3 volt voltage under the temperature of 750°C. Reaching the aim temperature need 3 hours then totally 6 hours for balance and dissociation. The electrolysis time after calculation was around 6 hours. Then as same as the big scale experiment, the electrodes were washed after cooling to the room temperature and samples were tested.

4. RESULTS AND DISCUSSION

4.1 Big scale experiments
Some preliminary experiments were done for the big scale experiment. The ammeter was on before pushing the electrodes down to the molten salts. The initial current for the electrolysis was around 2.3A. Then the current had a slowly decrease then showed a wave change. Theoretically, the current will decrease to a very low level after all the ions change to metal phase under the fixed temperature and voltage. Then the experiment can stop and cooling down. Here is another interesting phenomenon during the experiment. When the current was at a lower level, shaking or moving up and down with the electrodes can make the current increase but in a short time the current fall back again. This may because of the attachment on the electrodes has some change such as some slats detached or some surface reactions happened.

There also some drawbacks during the procedure. As we know, AlCl₃ has a very low vaporization temperature, around 178°C. But around the top of the container, especially in the exhaust tube, it is cooled down and crystallized which can cause the block of the tube. Then the inside pressure will increase due to the generation of the gas. This situation lead to the rubber stopper for sealing the electrodes jump up and could also bring some security risks. To deal with this block, we use some heating element to heat the exhaust tube around 200°C to make the AlCl₃ into the gas washing bottle in gaseous form.

The pressure change in the container could lead another risk that the solution in the gas washing bottle may be sucked backward which is very dangerous when the temperature is high. So we use two gas washing bottles for the exhaust. The one near the container is empty and the other one has the solution inside. Also the argon flow rate can be increase during the cooling.

4.2 Lab scale experiments
The lab scale experiments are also some preliminary ones which show the feasibility of this electrochemical method used for recovery Mn.

The initial current for this electrolysis procedure was around 0.5A. The wave curve of the current was recorded but not as obviously as the big scale experiment. The electrode shake phenomenon also exists.
The current increased after moving of the electrodes. But there was no block of the exhaust tube. Some
typical pictures about the Mn extraction experiment are shown below.

![Fig 5. Typical photos of the cathode products from Mn electrolysis. a) Before washing; b) After washing; c) Collected powder.](image)

Figure 6 shows a typical SEM photo of the electrolytic Mn from MnO. From the picture we can see the
dark phase and the bright phase. EDS analysis showed that the bright phases have the manganese
content around 95wt%. There is also some chlorine and sodium left which may due to the not washed
salts.

![Fig 6. A typical photo of SEM](image)
5. CONCLUSION AND FUTURE WORK

In this paper, electrochemical method was used for both Cr and Mn recovery. Both extraction and electrolysis is done with industrial slag and pure MnO.

From the results of the industrial experiments, this method needs to be improved with both the equipment and the parameter optimization. Firstly, the more serious problem is the block of the exhaust. On one hand, it is AlCl$_3$ phase change that makes the block so that the amount of AlCl$_3$ should be decrease or find other flux to instead.

From my colleague’s study [8], there are several methods could be used in the improvement. a) Add LiCl in the salts system. Study shows that the adjunction of LiCl in the system can not only decrease the electrolysis temperature but also increase the current; b) Use aluminum powder as the anode. The method is very effective in the lab scaled experiment which can substantially reduced the use of the AlCl$_3$. Since the produced Cl$_2$ gas will react with molten salts as well, only small amount of AlCl$_3$ is needed at the beginning of the electrolysis. Even these two methods works, there still will be vaporization in the system. So on the other hand, some methods should be used to deal with the solidification of the volatile. We have already tried the heating of the exhaust tube and the results shows it works well, so we will keep this solution in the future work. And also, the tube size for the existing equipment seems too small, if the big size tube used in the further more experiment the block maybe lighten.

For the suck backward of the CaO solution, two gas washing bottles series connection seems work well. But if some solid adsorbent could be used for the exhaust then it will be safer.

It has to be mentioned that the composition of the industrial slag is so complex that not so suitable for determine the parameters.

And also the distance between the electrodes for the big scale electrolysis seems a little large now. One solution is to use some big size part at the end of cathode. Not only it can decrease the distance but also increase the surface area of the cathode and decrease the current density. These are all benefits for electrolysis.

The results for the lab scale experiments are quite well. It shows this extraction with electrolysis could be used for Mn recovery. Even though, further work should be done to optimize the parameters so that the energy consumption and the yield of the Mn product can be balanced. From the experience of the big scale experiments, LiCl$_2$-NaCl-KCl system and Al powder electrode should also be tested in the Mn recovery in further.

Another thing need to take care in the further work is that all these products from this electrochemical method are very active metals. That means they are very easy to be oxidize again. So the washing for the deposition should be taken carefully and additional protective method should be used on the products. And also analysis for the products should be taken right after the experiment.

The work done in this paper shows that there is potential of this electrochemical method in recovery of the elements. This is good news for the environmental protection and resources conservation.
6. ACKNOWLEDGMENTS

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7. REFERENCES