

Optimization of Salt Extraction Process through cyclic production and consumption of aluminium chloride by a novel anodic reaction

Babak Khalaghi*, Lidong Teng and Seshadri Seetharaman

Dept. Materials Science and Engineering, Royal Institute of Technology, Stockholm, Sweden

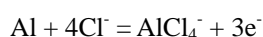
Abstract: The present work presents the development and optimization of “salt extraction process” which has been previously used for recovery of valuable metals from slags and ores. In our previous studies on this process the extraction of metallic values were carried out through utilization of aluminium chloride (AlCl_3) which acts as flux in the process. This however leads to high consumption of AlCl_3 . Present work introduces the new electrolysis system in which the required AlCl_3 is produced *in-situ* by the modification of the electrode reactions. This had the added advantage of eliminating chlorine evolution during electrolysis. For this, electrolysis experiments were carried out on EAF slag for the recovery of chromium. SEM/EDS and XRD analyses of the cathode deposit confirmed the deposition of CrFe alloy on the cathode by the modified technique.

Key words: Salt extraction process, electrode reaction, AlCl_3 formation, chromium recovery

1. Introduction

Metallic chromium can be obtained by electrolysis whether in aqueous or molten salt media. However, when chromium is electrodeposited in aqueous media there is always hydrogen evolution and that the process produces a lot of waste materials which may contain Cr (VI) species. On the other hand, deposits obtained in molten salt media have shown good adherence and that there is no need for further purification. Consequently, molten salt processes seem to be superior to aqueous ones [1, 2]. So far many studies have been done using different mixtures of salts. Some of the more important of such studies include electroplating of chromium from $\text{LiCl}+\text{KCl}$ by direct and pulsed current electrolysis [2], preparation of chromium powder by “FFC Cambridge Process” [3], electrochemical studies of Cr chlorides in $\text{LiCl}+\text{KCl}$ [4]. Any chromium production process is more advantageous and worthy if it is capable of using raw materials with lower purity (such as chromium-containing ores and waste materials) and that there is no need for any pre-treatment process. In an attempt to come up with such process “Salt Extraction Process” was developed [5, 6]. This process is based on the principle of “leaching of the metal values” from raw/waste materials. In this process, the slag or the other raw/waste material (containing the desirable metal) is dissolved into the molten salt phase at a suitable temperature. In fact, dissolution or extraction here means that the oxide containing the desired metal is chloridized and then this chloride enters the salt mixture. After extraction (dissolution), the salt bath (containing the ions of the metal) is subjected to electrolysis and desired metal is recovered as a cathode deposit. This process has been applied to Electric Arc Furnace (EAF) slag for recovery of Cr and also to copper concentrate for copper extraction and has shown quite promising results were obtained. In the salt extraction process, aluminium chloride (AlCl_3) is used as chloridizing agent [5]. But due to its high vapour pressure a large amount of it evaporates before it can effectively chloridize the oxides.

In order to overcome this problem, the process has been redesigned, by a novel idea, in a way that the necessary aluminium chloride needed for the extraction is generated *in-situ*. In this modified process the metallic aluminium acts as anode and aluminium chloride or alkali chloroaluminates are formed as a result of anodic dissolution of aluminium in chlorides melt. This aluminium chloride complex then reacts with the oxides in the system and chlorinates them. Then it is followed by electrochemical reactions of these newly formed chlorides on electrodes which results in the deposition of desired metal on cathode and simultaneously reaction of chlorine ions with metallic aluminium at anode i.e. aluminium dissolution. The electrochemical dissolution of aluminium in such melts can be presented by the following reaction [7, 8]:



As long as metallic aluminium and desired metallic oxides are available the process can continue by these cyclic reactions.

2. Experimental

Two series of electrolytic experiments were done. In the first series a little amount of aluminium chloride was added from the beginning to start the process. As the electrolysis begins, aluminium chloride is produced *in-situ* and the necessary amount of AlCl_3 is provided as the process continues. In second series of experiments the process was started by electrolysis of KCl/LiCl . In this way some aluminium chloride and/or chloroaluminate complexes are generated which can later chlorinate the metallic (Cr, Fe) oxides in the system. After electrolysis of KCl/LiCl the applied voltage was changed and the process was continued with electrolysis of chromium chloride and iron chloride.

Powders of KCl , LiCl , NaCl , Cr_2O_3 and FeO (all anhydrous, $\geq 99\%$ purity, Sigma Aldridge) were weighed and mixed. Amounts of alkali chlorides were based on the composition of the triple eutectic point in the KCl-LiCl-NaCl phase diagram which is in fact the electrolyte composition. Mixture of alkali chlorides, chromium oxide and iron oxide along with the alumina crucible (99.5 %, 40 mm i.d., 60 mm o.d., 60 mm height, from Keranova AB Sweden) were dried at 110°C for 24 h. After drying, first aluminium powder ($\geq 99\%$ purity from Alfa Aesar) and after that the dried, mixed powders were poured into the alumina crucible. In experiments where aluminium chloride was used the weighed amount of AlCl_3 (anhydrous, $\geq 99\%$ purity, Sigma Aldridge) was added to the rest of chemicals at this stage. Then the crucible containing the chemicals was placed into the alumina tube of the vertical furnace and it was heated up to 850°C while the electrolyte was blanketed by flowing argon gas introduced from the bottom of the furnace tube. Two graphite rods were used as electrodes. These were placed just above the crucible while heating up the crucible. To start the electrolysis the graphite rods were pushed into the crucible. Since aluminium has a higher density than the salt bath it remains at the bottom of the crucible after melting. Therefore, the graphite rod which served as the cathode was pushed down enough to dip into the electrolyte but not to reach the molten aluminium at the crucible bottom. On the contrary, the one serving as anode was pushed down until it was placed in the molten aluminium. This graphite rod which was used as anode had been tightly passed through an alumina tube in way that only few millimeters of rod's tip was exposed to aluminium and the rest was protected from the electrolyte. Electrolysis was performed at constant voltage at 1.5 V. For second series of experiments the process was started by electrolysis of KCl/LiCl for 3 h at 5 V and later at 1.5

V for 3 h. The potential was supplied by DC power (hp Hewlett 6632A). After electrolysis the electrodes were cooled down inside the furnace and under protection of argon gas. The cathode deposit was washed by distilled water and ethanol and later examined and analyzed by SEM /EDX.

3. Results

Figure 1 shows the deposit on cathode after the electrolysis procedure for first series of experiments. As mentioned earlier, this sample contained a little amount of aluminium chloride from the beginning. This initial amount initiates the process. As it seen in the SEM image (down-left) three phases can be distinguished. According to EDX chemical analysis the area labeled by 1 is the metallic phase with composition of Al 56, Cr 24, Fe 17 and O 1,3 (wt. %). The second phase (labeled 2) is almost pure aluminium (Al 95 wt. %) and the area no. 3 is composed of remaining alkali chlorides and aluminium oxide on the deposit. Similar phases and areas were detected in other samples. The other images in Fig. 1 correspond to mapping of chromium, iron and aluminium in the same area of the sample. It is clear that iron and chromium appeared in the same areas. This illustrates the co-deposition of iron and chromium. Also deposition of aluminium is obvious.

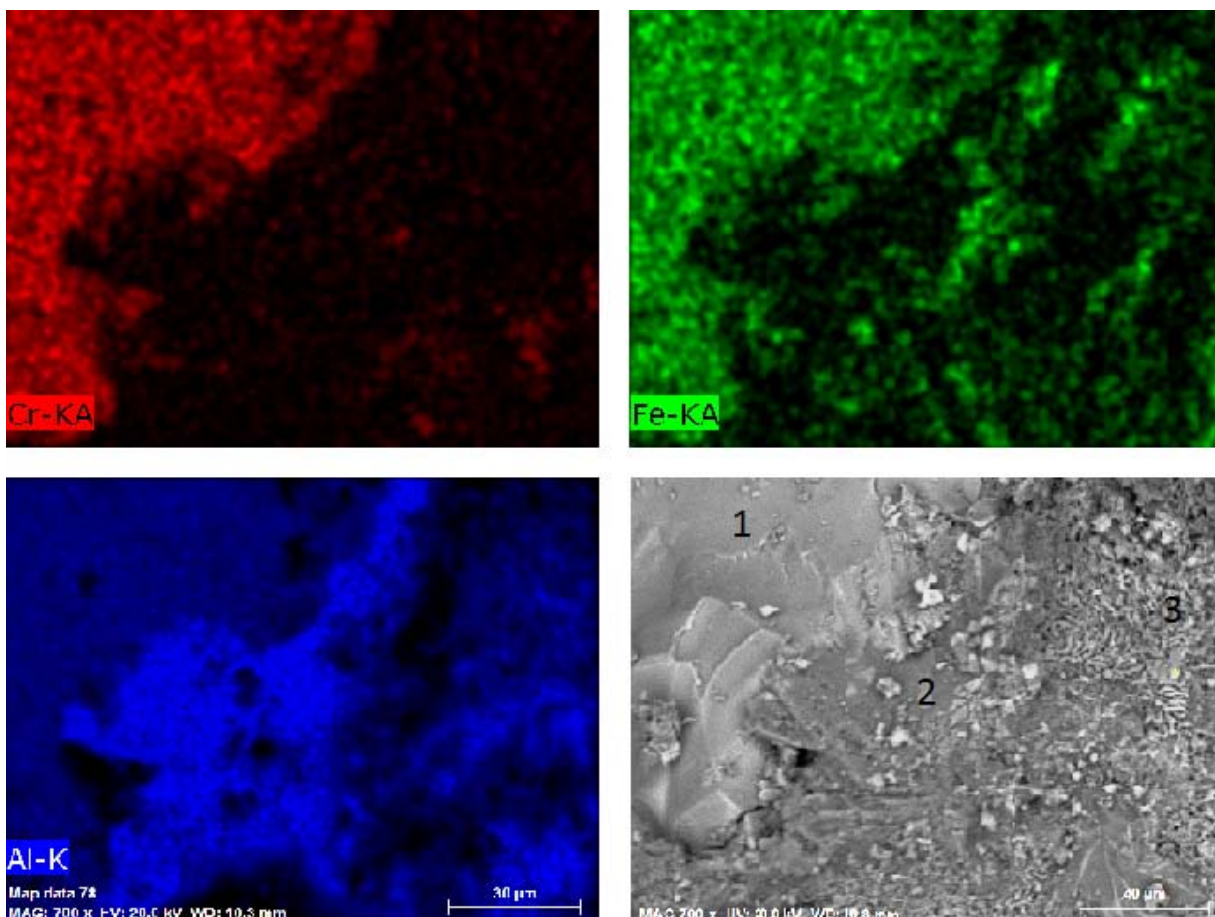


Fig. 1 SEM image of cathode deposit and mapping of the same area for chromium, iron and aluminium; little amount of AlCl_3 was added

Figure 2 illustrates the SEM images of a sample from second series of experiments. As mentioned before, for this sample no AlCl_3 was added from the beginning and the process initiated by deposition of alkali metals in the system (K, Li) at 5 (V). This generated some AlCl_3 or chloroaluminate complexes in the system which then reacted with chromium oxide and iron oxide. After some time the potential was decreased to 1.5 (V). Therefore, deposited alkali metals were stripped from the cathode and deposition of chromium and iron occurred. The image on the right shows the deposited metals on cathode plus some aluminium oxides particles (marked by arrows). The composition of the metallic phase (matrix) is Al 65, Cr 20, Fe 14 and O 1,4 (wt. %) which is similar to previous sample. However, the composition was a little different in some other samples in this second series of experiments. For example in Figure 2 (left) the metallic phase (bright areas) contains less aluminium (28 wt. %) and chromium (10 wt. %) and more iron (around 60 wt. %). Darker areas (grey) are those parts of deposit which is covered by remaining alkali chlorides.

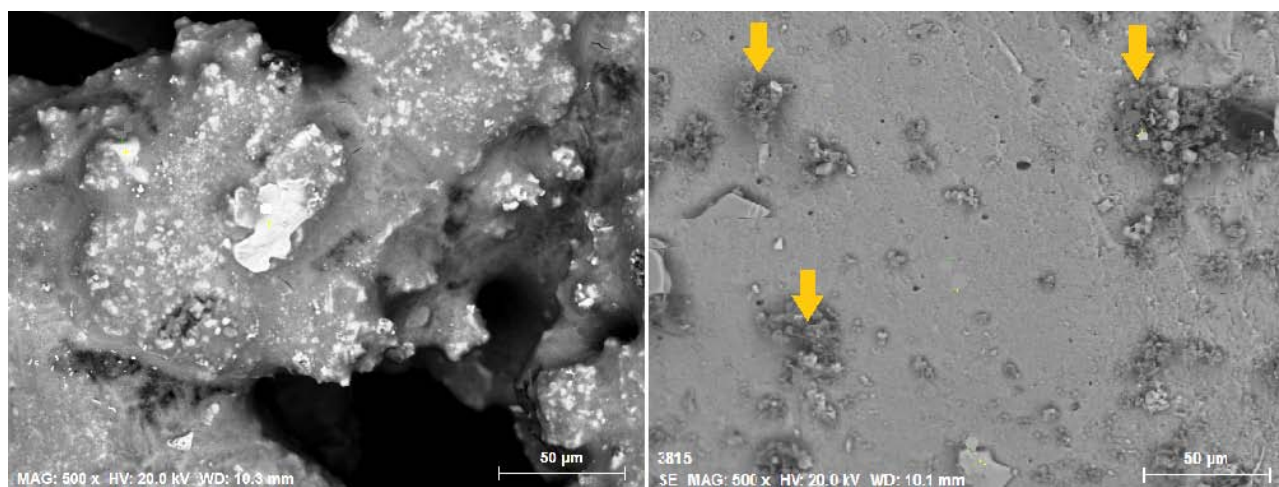


Fig. 2. SEM images of cathode deposit; no AlCl_3 was added.

4. Discussion

Chemical compositions of deposits on the cathodes presented in Fig. 1 and Fig. 2 confirm the deposition of chromium and iron. The potential applied in this process was 1.5 (V). Theoretical value of deposition voltage for CrCl_3 is at this temperature is around 1 (V) assuming the evolution of chlorine gas in the deposition reaction. Then considering the overpotential, in practice the applied potential is around 2.8 (V) [5]. However, if in the deposition reaction chlorine gas is replaced by aluminium chloride then the theoretical deposition potential is equal to -0.7 (V) which becomes positive when the overpotential is added. Here, the applied potential was chosen 1.5 (V) assuming that dissolution of aluminium at anode and considering the overpotential. And as it seen from the results this has ensued in deposition of chromium and iron which shows that the reaction involved generation of AlCl_3 . Deposition potential of FeCl_3 is very close to CrCl_3 . This is why co-deposition of iron and chromium has occurred (mapping in Fig. 1). This co-deposition was also detected in previous studies [5]. Furthermore, as can be seen in Figure 1 aluminium has also deposited on the cathode. This is probably because of abundance of aluminium in the system and that the chosen applied potential is close to deposition voltage of AlCl_3 .

5. Conclusions

The so-called salt extraction process which is a method for recovery of metallic values from oxidic resources has been optimized by a novel design. In this process the recovery of desired metal is performed by chlorination of the corresponding oxide and successive electrolysis in molten salt media. Previously aluminium chloride which acts as the chlorinating agent was used as one the raw materials and was added from the beginning to the salt bath. But due to high vapor pressure it showed a low yield. In current study, the process has been optimized through a novel design which leads to in-situ generation of necessary aluminium chloride. Here the aluminium was used as the anode. Therefore, instead of chlorine gas evolution the anodic reaction leads to generation of aluminium chloride. Electrolysis experiments were done using this new design. The cathode deposits were examined by SEM and EDX. Chemical analysis confirmed the deposition of chromium and iron on the cathodes. From the deposition voltage applied it was proved that anodic reaction led to anodic dissolution of aluminium in chloride mixture. By applying this new design the aluminium chloride loss will be minimized and the process will be much more economical.

Acknowledgement

The authors wish to express their gratitude to the financial support from the Swedish Environmental Research Foundation (Mistra project 88034).

References

- [1] A.M. Martínez, Y. Castrillejo, B. Børresen, M.R. Bermejo, M. Vega, Chemical and electrochemical behaviour of chromium in molten chlorides, *J. Electroan. Chem.*, 2000, 493, p.1–14.
- [2] A. Cotarta, J. Bouteillon, J.C. Poignet, F. Vasiliu, V. Cotarta, Preparation and characterization of chromium deposits obtained from molten salts using pulsed currents, *J. App. Electrochem.*, 2001, 31 (9), p 987-995.
- [3] E. Gordo, G.Z. Chen, D.J. Fray, Toward optimisation of electrolytic reduction of solid chromium oxide to chromium powder in molten chloride salts, *Electrochim. Act.*, 2004, 49 (13), p 2195-2208.
- [4] A. Cotarta, J. Bouteillon, J. C. Poignet, Electrochemistry of molten LiCl-KCl-CrCl₃ and LiCl-KCl-CrCl₂ mixtures, *J. App. Electrochem.*, 1997, 27 p 651-658.
- [5] X.L. Ge, O. Grindler, S. Seetharaman, The salt extraction process: a novel route for metal extraction Part I – Cr, Fe recovery from EAF slags and low grade chromite ores, *Trans. Inst. Min. Metall. C: Mineral Processing and Extractive Metallurgy*, 2010, 119 (1), p. 27-32
- [6] X.L. Ge, S. Seetharaman, The salt extraction process: a novel route for metal extraction Part 2 – Cu/Fe extraction from copper oxide and sulphides, *Trans. Inst. Min. Metall. C: Mineral Processing and Extractive Metallurgy*, 2010, 119 (2), p. 93-100.
- [7] Q. Li, N.J. Bjerrum, Aluminum as anode for energy storage and conversion: A review, *J. Pow. Sor.*, 2002, 110 (2), p. 1-10.
- [8] L.G. Boxall, H.L. Jones, R.A. Osteryoung, Solvent equilibria of AlCl₃-NaCl melts, *J. Electrochem. Soc.*, 1973, 120 (2), p. 223-231.