INVESTIGATION OF A MOLTEN SALT EXTRACTION/ELECTROLYSIS PROCESS FOR CONVERTING ILMENITE TO IRON AND A HIGH GRADE TiO₂ FEEDSTOCK

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The feasibility of beneficiating (upgrading) ilmenite ores using a molten salt extraction/electrolysis process was investigated. In this process, the iron fraction is selectively extracted from ilmenite and reduced to metallic iron at the cathode; the oxygen species is converted to CO and/or CO₂ at a carbon anode. The beneficiated (upgraded) ore is then recovered from the melt, and the molten salt is recirculated back to the reactor. The high TiO₂ content of the ore after extraction of the iron fraction increases its value as a feedstock for the production of TiO₂ pigment by the Chloride Process. Several salt systems were studied, including LiCl-KCl, NaOH-KOH, LiBO₂-KBO₂, and LiCl-KCl-LiBO₂. Of these systems, the best results were obtained for the LiCl-KCl-LiBO₂ system containing 5 to 20 weight % LiBO₂.

INTRODUCTION

In 1991, approximately 1.4 million tons of TiO₂ pigment were produced worldwide using the Chloride Process (1). In this process, titanium ores are chlorinated in large fluidized beds to produce TiCl₄, which is purified and then oxidized to produce pigmentary TiO₂ particles (2). In the chlorination process, the majority of the ore impurities, predominantly iron, are also chlorinated and subsequently separated from the TiCl₄. To minimize the generation of metal chloride wastes, it is desirable to remove the impurities prior to chlorinating the ore.

Background

A variety of beneficiation routes for titaniferous ores have been reported in the literature (3,4) yet there are only three major commercial beneficiation routes practiced today: slagging (5), reduction-rusting (6,7), and reduction-leaching (8). In the slagging process, the grade of the TiO₂ product is generally below 86 %, and the slags often contain significant quantities of CaO from the coke used as the reductant. High CaO levels can cause operational difficulties in fluidized-bed chlorinators (9). Both the reduction-rust and reduction-leach processes produce a much higher grade TiO₂ product (90 - 95 % TiO₂) with low CaO levels, but generate a large amount of iron oxide waste. Thus, there is a
need for a low cost beneficiation process to produce a high grade TiO$_2$ feedstock (> 90 % TiO$_2$) with minimal production of waste.

In an effort to develop a superior beneficiation process, a variety of molten salt routes have been investigated. In 1956, a patent was granted to Columbia-Southern Chemical Corporation for a process in which molten NaOH was used to convert ilmenite to a solid phase enriched in iron and a liquid phase enriched in TiO$_2$ (10). However, the process resulted in the formation of sodium titanates, resulting in high NaOH consumption and an unacceptably high Na-content in the TiO$_2$ product. In 1989, Heikel received a U.S. patent (11) for a process in which NaOH was used to produce sodium titanate which was then leached with HCl to form an amorphous TiO$_2$·nH$_2$O product. The amorphous titania could be calcined to produce a high grade TiO$_2$ product; however, the high NaOH consumption and the need to treat the resulting acid stream make this a very expensive process. A substantial amount of effort has also been focussed on molten salt chlorination processes in which the ilmenite ore is reacted with Cl$_2$ in a molten chloride bath (12-15). However, such processes do not eliminate the chloride waste problem.

A molten salt extraction/electrolysis process could potentially avoid the problems of high salt consumption and waste generation. In this process, the iron fraction would be selectively extracted from the ilmenite and deposited as metallic iron at the cathode. Such a process should be capable of making a 90 - 95 % TiO$_2$ product similar to that obtained from the reduction-rust and reduction-leach processes. However, unlike the latter two processes, a valuable iron coproduct would be produced instead of an iron oxide waste.

Choice of Molten Salt System

A distinct advantage of molten salt systems over aqueous systems for electrolytic deposition of metallic iron is the high decomposition voltages associated with molten salt systems which makes it possible to control the cathode at a potential sufficiently negative to produce iron at reasonable rates without decomposing the salt. A number of molten salt systems may be envisioned; the specifications for an ideal salt system are listed below.

1) The solubility of the iron fraction of ilmenite in the melt should be high at relatively low temperatures while the TiO$_2$ fraction is insoluble.

2) The molten salt should be non-viscous and allow for high transport rates of the dissolved species to the electrodes, as well as allow rapid evolution of CO and/or CO$_2$ from the anode.

3) The salt should not react with the metallic iron product and should be easily washed free from both the iron and TiO$_2$ products.

4) For a low-cost process, the salt needs to be economically recovered and recirculated back to the process with minimal consumption.
EXPERIMENTAL

Ilmenite

Two different ilmenite sources were used in this investigation: 1) synthetic ilmenite, FeTiO$_3$, containing 53 weight % TiO$_2$, and 2) partially reduced Florida Ilmenite (PRFI) containing 67 % TiO$_2$. In both cases, the iron is predominantly present as Fe$^{+2}$. The synthetic ilmenite was prepared by heating a stoichiometric ground mixture of Fe$_2$O$_3$ and TiO$_2$ under a helium atmosphere to 1150 C for 12 hours, cooling, grinding, heating for 24 hours at 1150 C, cooling, grinding, and heating an additional 12 hours at 1150 C. Only ilmenite was present in the X-ray diffraction pattern. The PRFI sample was prepared by heating Florida Ilmenite (65 % TiO$_2$) for 8 hours at 1000 C under an atmosphere with a CO/CO$_2$ ratio of 0.1 to convert the iron to the Fe$^{+2}$ state.

Solubility Studies

A schematic of the apparatus used for conducting the solubility experiments is shown in Figure 1. In a typical experiment, 300 - 400 grams of salt were added to an Al$_2$O$_3$ crucible inside a quartz tube. A pyrex cap equipped with two ports for gas inlet and exit, as well as a sampling port was attached to the top of the quartz tube via a 75 mm joint. The system was purged with either 200 scm of helium or 10 % CO in helium, and heated to the desired temperature over a 2 hour period with a crucible furnace. The gas entered the reactor through a hollow Al$_2$O$_3$ tube which could be raised or lowered. Once the salt was melted, the Al$_2$O$_3$ tube was lowered into the melt, and the salt was sparged for 1 hour. Then the Al$_2$O$_3$ tube was lifted out of the melt, and a nickel crucible was lowered into the melt through the sampling port. Approximately 25 g of the melt were removed and poured into a dry stainless steel beaker. The beaker was placed in cold water to quench the melt, and the frozen salt was broken up and placed in a sample bottle which was immediately weighed and then placed in a dessicator. This sample served as the control sample.

After taking the control sample, 30 - 40 grams of ilmenite ore were poured into the melt through the sampling port. The melt was sparged for 1 hour, and then the solids were allowed to settle for 20 minutes before taking a sample of the melt. Once the sample was taken, the system was heated over a 1 hour period to the next desired temperature. After sparging for 1 hour at temperature and then allowing the solids to settle for 20 minutes, another melt sample was taken. This procedure was repeated until a sample was taken at each desired temperature. The next day, a small portion of each sample was weighed, dissolved in HCl, and then analyzed by ICP (Inductively Coupled Plasma Spectroscopy).
Electrochemistry Experiments

A schematic of the apparatus used for the electrochemistry experiments is shown in Figure 2. 100 grams of salt were added to an Al₂O₃ crucible which was placed inside a quartz tube. The quartz tube was covered with a pyrex cap containing 2 ports for electrodes and a third port for gas inlet. The cathode consisted of an 8 cm long piece of 0.5 mm diameter Pt wire folded in a tight loop around a Pt lead wire so that the total length of the electrode was 4 cm. The Pt lead wire was passed through a hollow Al₂O₃ tube up through the port on the pyrex cap and connected to the potentiostat lead via an alligator clip. The anode consisted of a 4 cm long, 6 mm o.d. graphite rod. A spiral groove was cut at the top of the rod, and the Pt lead wire was wound tightly into the groove to hold the electrode. A 2 mm Ag wire was used as a quasi-reference electrode in each case. The Ag wire was also attached to a Pt lead wire. The Pt lead wires for the anode and reference electrode passed through 2 separate holes in an Al₂O₃ disk, and then up through separate holes in the same piece of 4-hole Al₂O₃ tubing as shown in Figure 2.

The salt was heated to the desired temperature under a He or CO/He purge, and sparged for 1 hour. The electrodes were then inserted into the melt to a depth of 4 cm, corresponding to approximate electrode areas of 1.3 cm² for the Pt electrode, and 7.5 cm² for the graphite electrode. Several cyclic voltammograms were run to characterize the melt in the absence of any ore. Then after removing the electrodes 20 grams of ore were poured into the melt. After sparging 1 hour and allowing the solids to settle for 20 minutes, the electrodes were immersed in the melt, and the electrochemistry experiments performed.

An EG&G PARC Model 270 Electrochemical Analysis system was used to conduct the electrochemistry experiments. This system consisted of a Model 273 Potentiostat/Galvanostat interfaced to an IBM PS/2 Model 30 computer.

RESULTS AND DISCUSSION

LiCl-KCl System

In beginning an investigation of a molten salt extraction/electrolysis process it was desirable to start with a system that was relatively well understood in order to gain some confidence with respect to the results obtained. The chemical and electrochemical properties of Ti-O and Fe-Ti-O compounds in the molten LiCl-KCl eutectic (44.4 weight % LiCl) at 470 C have been described by Ferry, et al. (15) and by Picard, et al. (16). An interesting property of this system is that Fe²⁺ is far more soluble in the chloride salt than Fe³⁺ or Ti⁴⁺. Thus, it was felt that partial reduction of the iron fraction of ilmenite to Fe²⁺ would allow selective extraction of the iron. However, a disadvantage of this system is that the solubility of Fe²⁺ oxides is not very high in chloride salts.

The measured solubility of the iron fraction of ilmenite as a function of temperature

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is shown in Figure 3 for both synthetic ilmenite and the partially reduced Florida Ilmenite (PRFI). For these experiments, the system was constantly purged with a mixture of 10 % CO in He to maintain a low oxygen activity in the melt. For both ilmenites the solubility of the iron fraction increases exponentially with temperature. In each case, less than 1 ppm of titanium was detected in the salt indicating high selectivity for iron over titanium. Due to the higher solubility of Fe$^{+2}$ from the PRFI sample at 800°C, the electrochemistry experiments were conducted using this ilmenite sample.

Cathodic cyclovoltammograms (CV's) for PRFI in LiCl-KCl at 800°C are shown in Figure 4 for a platinum working electrode at sweep rates of 0.02 and 1.0 V/s. For reference, the CV for the LiCl-KCl in the absence of any ore is also shown. A reduction peak was observed between -0.2 and -0.4 V vs. the Ag quasi-reference electrode. The location of this peak was right where the reduction peak for the conversion of Fe$^{+2}$ to Fe$^0$ was expected to occur (15). This peak assignment was confirmed as follows. The cathode potential was stepped to -0.25 V and held there for 1 hour. The cathode was then removed, and a black, highly magnetic material resembling iron filings was removed and analyzed by SEM/EDAX (Electron Diffraction Analysis of X-rays using a Scanning Electron Microscope). The material analyzed as 81 % Fe, 1 % Ti, 9 % K, and 9 % Cl. The K and Cl were due to the fact that the iron was not washed well before analyzing. The titanium was most likely due to the presence of a small amount of ore in the iron deposit.

An anodic cyclovoltammogram (CV) for PRFI in LiCl-KCl at 800°C using a graphite working electrode is shown in Figure 5 for a sweep rate of 0.1 V/s. This CV was virtually identical to what was obtained for LiCl-KCl in the absence of ilmenite. The break at approximately 1 V corresponds to where the oxidation of Cl$^-$ to Cl$_2$ would be expected to occur (15). The lack of any peaks attributable to the reaction of oxyanions with the carbon electrode suggests that during deposition of metallic iron at the cathode, the corresponding anodic reaction is most likely the conversion of Cl$^-$ to Cl$_2$. This may explain the secondary cathodic reaction that is evident in Figure 4 at potentials more negative than about -0.25 V.

As the potential at the cathode becomes more negative, the deposition rate of iron increases, as does the evolution rate of Cl$_2$ at the anode. It is possible (although not confirmed) that the Cl$_2$ generated at the anode diffuses to the cathode where it is either reduced, or reacts with the metallic iron to form FeCl$_2$ which dissolves in the melt. In the latter case, the reaction with Fe would replenish the level of Fe$^{+2}$ in the boundary layer near the cathode and prevent the reduction reaction from becoming completely mass transfer-limited. As a result, a definitive peak would not be obtained. Similarly a definitive peak would not be obtained if the Cl$_2$ were just being reduced directly at the cathode. Instead, the cathodic current would continue to rise as the overpotential was increased. The higher reduction rate at the cathode would be largely balanced by a higher production rate of Cl$_2$ at the anode. Thus, at potentials more negative than -0.25 V, the apparent current density increases, but the net production of metallic iron at the cathode does not increase. This hypothesis is supported by the experimental observation that deposition of iron at potentials more negative than -0.25 V did not increase the yield of Fe at the cathode, despite the fact that the measured current densities were very different. At -0.25 V vs. the Ag quasi-reference electrode, the measured current density was approximately 0.01 A/cm$^2$, of which only about half corresponded to the net reduction of Fe$^{+2}$ to Fe$^0$. 

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The results presented above show that for ilmenite in the LiCl-KCl system, the iron deposition rate at the cathode is relatively low, and the reaction rate of oxyanions with the carbon anode is extremely low. These low rates can be attributed to the low solubility of oxides in chloride systems. Thus, it was decided to investigate the use of oxygen-containing salts. One class of oxygen-containing salts which also can easily be washed from the products and recovered are the alkali hydroxides. An added benefit of the hydroxide systems is that they are low melting. Therefore, it was decided to investigate the electrochemical behavior of ilmenite in the NaOH-KOH eutectic.

NaOH-KOH System

An interesting property of the alkali hydroxides is that the chemical properties of these melts are a strong function of the water content, or acidity (17-20). In general, under wet (acidic) conditions, metallic oxides react with the water and dissolve as cations plus hydroxide ions (e.g. FeO + H₂O = Fe⁺² + 2 OH⁻). As the melt is dried, the solubility decreases due to the lack of availability of water for reaction. When the melt is dehydrated still further, the solubility goes through a minimum and then increases again. Under dry (basic) conditions, the metal oxides generally dissolve as alkali-metal-oxide salts (e.g. Fe₂O₃ + 2 NaOH = 2 NaFeO₂ + H₂O) which are usually highly soluble.

The simplest way to vary the water content of the hydroxide melt is to start with a hydrated melt and heat it to drive off the water. As the temperature is raised, the melt becomes more dehydrated and thus, more basic. The solubility of synthetic FeTiO₃ in NaOH-KOH was measured under acidic (wet) and basic (dry) conditions. In these experiments, a mixture of 185 g KOH·0.5H₂O and 115 g of NaOH was heated to 250°C, during which time some steam was observed in the exit from the reactor. After taking a “blank” sample, 30 g of synthetic FeTiO₃ were added to the melt and sparged with 200 cc/min of dry helium for 1 hour. After settling for 20 minutes a sample was taken as described above. The melt was then heated over 1 hour to 350°C, during which time a substantial amount of steam was observed in the reactor effluent. After 30 minutes, no more steam was evident, and the melt was considered relatively dry. After an hour, another sample of the melt was taken. The measured solubility of FeTiO₃ in the NaOH-KOH mixture is shown in Table I for 250°C (wet) and 350°C (dry).

| Table I              |
|---------------------|
| Solubility of FeTiO₃ in NaOH-KOH |
| Temperature (°C) | Fe  | Ti  |
|-------------------|-----|-----|
| 250               | 0.7 % | 0.4 % |
| 350               | 4.0 % | 3.0 % |

As seen in Table I, unlike the LiCl-KCl system, iron is not selectively dissolved vs. titanium in this system. However, an extraction/electrolysis system could still be
envisioned where the melt is saturated with titanium such that no more titanium dissolves, while iron is continuously dissolved and then deposited on the cathode. Because of the high soluble titanium loss at 350°C, it was decided to investigate the electrochemistry of this system at 250°C (wet conditions) where the soluble titanium loss is minimized. One possible problem which was anticipated with this system is that metallic iron is known to be oxidized by water and/or hydroxyl ions in aqueous hydroxide systems (21). Thus, it was expected that metallic iron might be oxidized in a wet (acidic) NaOH-KOH melt. However, it was hoped that by maintaining a sufficiently negative potential on the cathode, this reaction of metallic iron with the melt could be minimized.

Cathodic CV’s for synthetic FeTiO₃ in wet NaOH-KOH at 250°C are shown in Figure 6 for sweep rates of 0.02 V/s and 2 V/s. For comparison, the CV for the wet NaOH-KOH in the absence of ilmenite is also shown (sweep rate = 1 V/s). There is clearly a marked difference between the CV’s with and without ilmenite present. However, the fact that the CV’s with ilmenite present were nearly straight lines with no peaks, and that the sweep rate does not have a significant impact on the curves suggested that something was wrong. Initially, a short circuit was suspected, but it was quickly verified that this was not the case.

The strange appearance of the CV’s in Figure 6 for ilmenite in wet NaOH-KOH may be explained as follows. As the iron species were reduced to metallic iron at the cathode, the freshly reduced iron was then reoxidized by reaction with the melt. As a result, there was no depletion of iron cations in the boundary layer near the electrode. Therefore, the current was solely determined by the electrode potential, and not subject to mass transfer limitations. This explanation is consistent with the observation that after holding the cathode at a potential of -0.4 V relative to the Ag quasi-reference electrode for 30 minutes, no iron was observed on the cathode despite the fact that a steady current of 0.23 Amps was maintained.

The high reactivity of metallic iron with alkali hydroxides under acidic (wet) conditions makes it extremely difficult to develop an economical extraction/electrolysis process for this system. While the reactivity of metallic iron with the melt should be much lower under dry (basic) conditions, the high solubility of the titanium fraction in the melt under these conditions presents a problem. However, if a high steady-state level of titanium can be maintained in the melt without impacting the iron quality, this system may be worth investigating further.

LiBO₂-KBO₂ System

The next salt system chosen for study was the LiBO₂-KBO₂ (44 wt. % LiBO₂, 56 wt. % KBO₂) system. This system was chosen because it was expected to have a high solubility for oxides and a low solubility for metallic iron. The solubility of partially reduced Florida Ilmenite (PRFI) in the LiBO₂-KBO₂ system was measured in the same manner as described earlier for the other salt systems. In this case a helium purge was used throughout the experiment. The measured solubility of PRFI in the LiBO₂-KBO₂ melt at
850 °C is shown in Table II.

|       | Fe    | Ti    | Mn    | Mg    |
|-------|-------|-------|-------|-------|
|       | 1.13% | 512 ppm | 1.15% | 87 ppm |

It is clear from Table II that iron is not selectively dissolved relative to titanium to a high degree in this system. As a result, an extraction/electrolysis process using this system would either have to maintain a high steady-state level of titanium in the melt, or an additional processing step would be required for recovering the titanium values from the melt. Nevertheless, the solubility of ilmenite measured in this system was about an order of magnitude higher than in the LiCl-KCl system. This higher solubility was expected to be somewhat offset by a higher viscosity which would slow the mass transfer rate in the LiBO$_2$-KBO$_2$ system.

Cathodic CV's for PRFI in LiBO$_2$-KBO$_2$ at 850 °C are shown in Figure 7 for sweep rates of 0.02, 0.1, and 1 V/s. For comparison, the CV for LiBO$_2$-KBO$_2$ in the absence of ilmenite is also shown (sweep rate = 0.1 V/s). In the absence of ilmenite, no significant amount of reduction was observed until about -0.7 V vs. the Ag quasi-reference electrode. However, when PRFI was dissolved in the melt, a reduction peak was clearly evident between -0.4 and -0.6 V depending on the sweep rate. It was readily verified by examining the electrode deposit that this reduction peak corresponded to the deposition of metallic iron on the platinum electrode. The iron deposition rates observed in this system were substantially higher than those observed in the LiCl-KCl system.

Unlike the LiCl-KCl system, the anodic reaction between dissolved oxygen species appears to be favorable in the LiBO$_2$-KBO$_2$ system. Anodic CVs of LiBO$_2$-KBO$_2$ in the absence of ilmenite were performed at 850 °C using either the platinum electrode or the graphite electrode as the working electrode; the results are shown in Figure 8. When platinum was used as the working electrode, no oxidation of the melt occurred until potentials above +0.7 V vs. the Ag quasi-reference electrode were reached. The nature of this reaction was not investigated, but may have been the reaction of oxygen anions in the melt to produce O$_2$. In contrast, when graphite was used as the working electrode, oxidation began at potentials more positive than -0.3 V, and the current density was much higher than in the platinum system. Because this reaction involves the melt itself there is no peak in the CV since the reaction does not become mass transfer limited.

The results shown in Figure 8 suggested that a reaction was occurring between oxygen anions and the graphite electrode. This was verified by the fact that after prolonged reaction, the carbon electrode was clearly pitted. Since no measurements were made on the gas effluent, the nature of this reaction is not known for sure, but is believed to be the reaction of oxygen anions with the graphite to produce CO and/or CO$_2$. In the presence of ilmenite, the CV looked essentially identical. Thus, it is expected that in the LiBO$_2$-KBO$_2$ system the reduction reaction corresponding to the deposition of metallic iron at the cathode
could easily be balanced by an oxidation reaction to produce CO and/or CO$_2$ at the graphite anode.

Despite the relatively high cathodic and anodic current densities exhibited by the LiBO$_2$-KBO$_2$ system, there are several serious problems associated with using this system for an extraction/electrolysis process. The solubility of the titanium fraction of ilmenite is high in this system and there is a strong tendency to form titanates. X-ray diffraction analysis of the residue at the bottom of the crucible indicated that the major phase present was Li$_2$TiO$_3$. Moreover, it is very difficult to wash the flux off the iron product.

LiCl-KCl + LiBO$_2$

The results presented above show that iron can be selectively extracted from ilmenite and electrolyzed to produce powdered iron using a LiCl-KCl flux. However, the low solubility of the iron fraction of ilmenite in the melt results in a low deposition rate of metallic iron. Moreover, the anodic reaction between dissolved oxygen species and the graphite electrode is very slow in the LiCl-KCl system. In the LiBO$_2$-KBO$_2$ system, the solubility of the ilmenite is relatively high, resulting in acceptable iron deposition rates. It also appeared as if the anodic reaction between oxygen anions and the graphite electrode to produce CO and/or CO$_2$ occurred at a moderate rate. However, the high solubility of titanium and the tendency to form titanates combined with the difficulty of washing the LiBO$_2$-KBO$_2$ melt off the iron product combined to make this system unattractive.

Based on these results, it was postulated that if the positive results from the two systems could be combined while minimizing the negative results, it might be possible to develop a commercially viable extraction/electrolysis process. The most obvious way to combine the benefits of both systems was to add varying amounts of LiBO$_2$ to the LiCl-KCl system.

The effect of LiBO$_2$ addition on the cathodic CV’s of PRFI in LiCl-KCl at 800 C is shown in Figure 9. Adding just 5% LiBO$_2$ to the LiCl-KCl melt resulted in an order of magnitude increase in the size of the peak corresponding to iron deposition. Increasing the LiBO$_2$ level to 20% resulted in a further increase in the size of the reduction peak. It is interesting to note that the peak occurs at roughly the same potential vs. the Ag quasi-reference electrode as was observed in the straight LiCl-KCl system.

Anodic CV’s for LiCl-KCl-LiBO$_2$ at 800 C as a function of LiBO$_2$ content are shown in Figure 10 for a graphite working electrode (sweep rate =0.1 V/s). The curves were essentially identical when the ilmenite was present in the melt. When 5% LiBO$_2$ was added to the melt an oxidation reaction was observed starting near 0.1 V vs. the Ag quasi-reference electrode. The size of this oxidation peak increased substantially when the amount of LiBO$_2$ was increased to 20%. It is believed that the oxidation reaction that is occurring is the same as that in the straight LiBO$_2$-KBO$_2$ system; namely the reaction between oxygen anions and the graphite electrode to form CO and/or CO$_2$. 

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At first glance, it would appear that adding more LiBO$_2$ to the LiCl-KCl melt might yield even better results. However, when the LiBO$_2$ level reached 20% in the melt, it began to become more difficult to wash the melt off the iron product. Also, X-ray diffraction analysis of the residue at the bottom of the crucible showed the presence of Li$_{0.8}$Ti$_{2.2}$O$_{4.8}$. Thus, lower titanates begin to form at a LiBO$_2$ level as low as 20%. The problem increases as the LiBO$_2$ level increases.

**SUMMARY**

The results for the four salt systems investigated are summarized in Table III below. The best results were obtained for the LiCl-KCl mixture containing 5 to 20% LiBO$_2$. In this system the positive aspects of both the LiCl-KCl and LiBO$_2$-KBO$_2$ systems were combined. These results suggest that with the right salt system, an economic molten salt extraction/electrolysis process for converting ilmenite ores to a high grade TiO$_2$ feedstock and a saleable iron coproduct may be feasible.

| Salt System          | Positive Aspects                  | Negative Aspects                          |
|----------------------|-----------------------------------|-------------------------------------------|
| LiCl-KCl             | Selective extraction of Fe$^{+2}$  | Low solubility of iron Fe$^{+2}$ leads to low Fe deposition rates |
|                      | Salt is easily washed off products|                                           |
| NaOH-KOH (acidic)    | High ilmenite solubility at low temperature | Titanium is also dissolved |
|                      | Salt easily washed off product    | Electrodeposited iron is reoxidized by the melt. |
| LiBO$_2$-KBO$_2$     | High ilmenite solubility          | Titanium is also dissolved |
|                      | High rates of Fe deposition and CO evolution | Extremely difficult to wash salt off products |
|                      |                                 | Titanate formation |
| LiCl-KCl+LiBO$_2$    | High Fe deposition rate           | Anodic reaction to form CO/CO$_2$ is still relatively slow |
|                      | Salt easily washed off products   | Tendency to form titanates at high LiBO$_2$ levels |

Table III
**Summary of Results for the Four Salt Systems Investigated**
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Figure 1: Schematic of Apparatus Used for Solubility Measurements

Figure 2: Schematic of Apparatus Used for Electrochemistry Experiments

Figure 3: Solubility of the Iron Fraction of FeTiO3 and PRFI in LiCl-KCl

Figure 4: Cathodic CV's of PRFI in LiCl-KCl at 800 C. Also shown is the CV for plain LiCl-KCl without ilmenite (dotted line)
Figure 5: Anodic CV of PRFI in LiCl-KCl at 800°C. Scan Rate = 0.1 V/s.

Figure 6: Cathodic CVs of FeTiO3 in NaOH-KOH at 250°C. Also shown is the CV for plain NaOH-KOH (1 V/s).

Figure 7: Cathodic CVs of PRFI in LiBO2-KBO2 at 850°C. Also shown is the CV for plain LiBO2-KBO2 (scan rate = 0.1 V/s).

Figure 8: Anodic CVs of LiBO2-KBO2 at 850°C for Pt and Carbon Working Electrodes. Scan rate = 0.1 V/s.
Figure 9: Effect of LiBO₂ Addition on Cathodic CV of PRTI in LiCl-KCl at 800 C. Scan Rate = 0.1 V/s.

Figure 10: Effect of LiBO₂ Addition on Anodic CV of LiCl-KCl at 800 C. Working Electrode = graphite, scan rate = 0.1 V/s.