

DISSOLVED METALS IN CRYOLITIC MELTS

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Abstract

A laboratory study was conducted for the determination of dissolved metals (including aluminum, sodium, and lithium) in cryolitic melts by using a tin extraction-stripping technique. Results demonstrate that the dissolved metal is not only aluminum, but actually a combination of aluminum, sodium, and lithium whose concentrations are dependent on the cryolitic composition and temperature. The results are shown to be rational and self consistent. Differences in total metallic solubility for earlier work in the literature can be attributed to the variations in experimental techniques. Metallic aluminum solubility increased with increasing bath temperature and decreased with increasing cryolite ratio (CR) and LiF concentration. Metallic sodium solubility increased with increasing CR and bath temperature, and decreased with increasing LiF concentration. Metallic lithium solubility increased with increasing CR, LiF concentration, and bath temperature, but was an order of magnitude less than the other metallic species. When molar CR was greater than 2.5, metallic sodium was the dominant component in the total solubility.

Introduction

Current inefficiency in primary aluminum production by the Hall-Heroult process is directly related to "back reactions" or dissolution and oxidation of aluminum in the cryolitic electrolytes. A proper understanding of the mechanisms of the back reactions or metal dissolution could possibly lead to further improvements in the technology of the Hall-Heroult process. Meanwhile, characterization of metal dissolution and determination of metal concentrations present in the cryolitic melts have been considered as critical steps in analyzing and formulating possible metal dissolution mechanisms.

Intensive investigations on the metal solubility in cryolitic melts have been carried out in the past several decades^[1 to 9]. However, no close quantitative agreement can be made except that researchers generally accept a solubility with a magnitude of 0.1 wt% aluminum exists in cryolitic melts. As concerning the measurements of individual solubilities of such metallic constituents as aluminum and sodium, no reliable techniques have been reported in the literature,^[2,8,9] and only several diverse and controversial data points for sodium concentrations in cryolitic melts are available. There is no information at all on metallic lithium solubility when LiF is added into the cryolitic melts. Lack of reliable metallic solubility data or individual quantities of aluminum, sodium, and even lithium dissolved in the cryolitic melts impedes further understanding the metal dissolution mechanisms and improving the current efficiency of Hall cells. Study of individual metal solubilities, therefore, not only has its theoretical importance, but also

relates to the practical significance of improving modern aluminum reduction technology.

This paper presents our laboratory study for the determination of dissolved metals including aluminum, sodium, and lithium in the cryolitic melts. A tin metal extraction-stripping technique was developed and first used in this metal solubility investigation. The tin metal extraction-stripping technique together with chemical analysis for aluminum, sodium, and lithium elements in the tin phase proved to be successful in distinguishing those species dissolved in cryolitic melts. The individual metallic solubilities could be experimentally determined. The extraction-stripping principle and its technical development for the solubility study will be reported separately elsewhere.^[10]

This paper covers only the results of individual solubilities of light metals including aluminum, sodium, and lithium in cryolitic melts obtained using the experimental technique. Effects of variables such as cryolite ratio, temperature, Al_2O_3 and LiF concentrations were determined and will be presented.

Experimental Methods

Test Equipment

Major test equipment used in this study included a vertical electrical furnace, specially-designed and manufactured crucibles, and quenching apparatus. The equipment and chemicals are described separately below.

Furnace. A vertical, electrical, resistance-wound Marshall furnace from Marshall Furnace Company, CA, was modified and used. It could be tilted right or left to any angle during the experiment. A schematic view of the furnace structure with a loaded crucible is shown in Figure 1. Both ends (top and bottom) of the furnace tube and the top removable tube lid were water cooled. Argon, as a protective atmosphere, was introduced into the furnace from the bottom. A VWR Vortexer 2 from Scientific Industries, Inc., N.Y., which is vertically movable by a lift support, was located beneath the furnace and was used as a vibrator to provide stirring for the sample by connecting to the crucible holder via a 1/4-inch diameter Inconel rod. The vibrator is turned on when the melts inside the crucible require stirring. The crucible and its cover were held in a graphite holder, which was suspended in the constant temperature zone of the furnace by a graphite rod. The temperature of the furnace was controlled by a West temperature controller, Model "2050" from West Division, Chicago. It was capable of holding temperature within $\pm 1^\circ C$ of a target temperature.

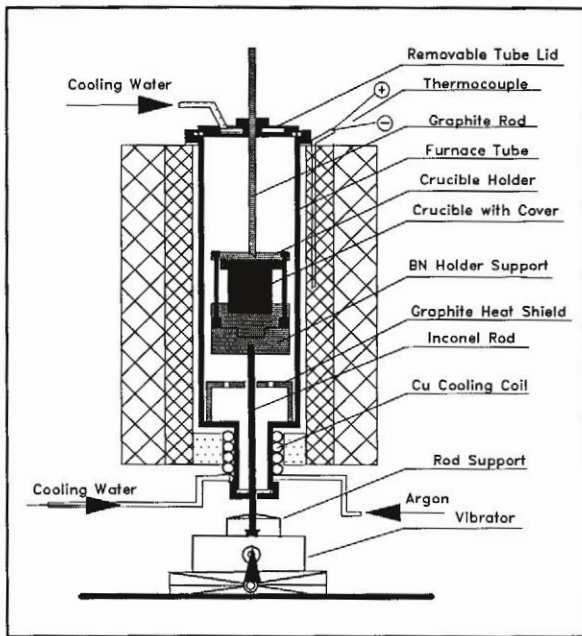


Figure 1: Schematic of the modified furnace with crucible system for dissolved metal studies.

Crucible. Boron nitride (BN) is one of a few materials resistant to the molten aluminum metal and cryolite corrosion. It does not wet with cryolite melts and metals involved in this study. HBR grade of BN from Union Carbide, OH, was used to make BN crucibles for the experimental determination of metal solubilities. The schematic diagram of the BN crucible specially designed for the study is shown in Figure 2. There were two

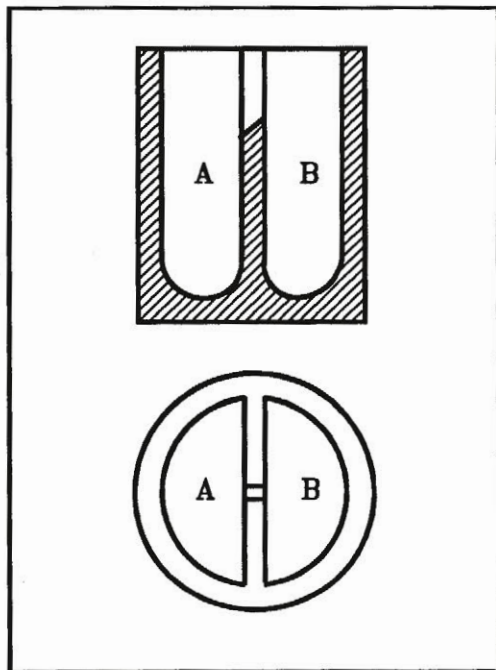


Figure 2: Schematic of two-chamber BN crucible used in the study of dissolved metals in the cryolitic melts.

deep wells acting as two individual compartments. In between the wells was a slot (with a sloped bottom) acting as a transfer passage for the melt when the crucible was tilted.

Sample-Quenching Apparatus. A fluidized-bed quenching method was selected and used in this study for its relatively fast rate to quench samples. The fluidized bed was filled with copper particles (-40 to +100 mesh) to form the bed and act as the heat sink. The bed was also water cooled with a copper coil inside the bed. Regulated compressed air was used to fluidize the copper particles and form a quench bed.

Chemicals. All chemicals used in this study were analytical grade without any further treatment. Cryolite (Na_3AlF_6) and aluminum fluoride (AlF_3), from CERAC, Inc. (Milwaukee, WI), and sodium fluoride (NaF) and lithium fluoride (LiF), from Fisher Scientific Company (Atlanta, GA), were predried at 110°C for at least 24 hours before use. A typically 99.9% pure tin in a 1/8-inch shot was obtained from CERAC, Inc. Impurities by spectrographic analysis are listed as follows:

Al	0.001%	Mg	0.001%
Ca	0.005%	Pb	0.11%
Cu	0.001%		

A grade of 99.95% pure aluminum in 1/2-inch pieces was obtained from ASAR, Inc. (Seabrook, NH). It was also directly used in the solubility measurements.

Experiential Procedures

Each experimental test for the determination of metal solubilities was conducted in the following manner. About 6 grams of high-purity aluminum was input in compartment A and covered by about 22 grams of prefused cryolitic sample. At the same time, about 10 to 11 grams of tin metal was loaded into compartment B. A marker for the compartment positions was also made on the outside the BN crucible wall before the BN lid covered the crucible. The crucible with its cover on was then mounted in the graphite crucible holder. This crucible system was then carefully loaded into the temperature-stabilized furnace in a specific direction. After 3 to 4 hours of equilibration, the furnace was then tilted 65 to 75 degrees for about one to two minutes to allow transfer of part of the metal-saturated cryolitic melt (about 9 to 12 grams) into compartment B. Once the furnace was back to its original position, the vibrator was immediately turned on for 1 hour. Then, 30 minutes of static equilibration was applied before the crucible system was quickly taken out of the furnace and quenched in the fluidized bed. The cryolite sample and the tin alloy phase in compartment B of the crucible were carefully removed, collected, and weighed on an analytical balance. Light metallic contents in the tin phase were analyzed on an ICP after digesting the alloy samples. The cryolitic sample left in compartment A was also collected for a mass balance check of the dissolved metallic species. At least two tests were carried out for each experimental condition. An experimental condition is one cryolitic melt composition at the temperature of interest.

Results and Discussion

The basic principle of the tin extraction-stripping method to measure the individual contents of light metals dissolved in the cryolitic melts is a two-step procedure. In the first step, a cryolitic melt phase and aluminum metal is equilibrated at the desired temperature. Then the remaining aluminum phase is removed and a new molten metallic phase such as tin of a known quantity is introduced into the light metal saturated melt. The second metal (such as tin) should be inert to the cryolitic melts. Once a new equilibrium state between the second metal phase and cryolitic phase is established, the system is quenched to ambient temperature. By chemically analyzing for the respective elements in the recovered alloy

phase, the concentrations of the light metals dissolved in the cryolitic melt can be obtained.

It has been established in partitioning tests of the light metals that a certain quantity of tin metal has to be introduced in order to strip over 95% of the light metals dissolved in the cryolitic melts.^[10] Experimental tests for the metal solubility were conducted following the established criteria of the light metals distribution between the tin and cryolitic melt phases. Individual solubilities of the metals in the cryolitic melts are calculated according to the following equations:

$$[m]_{\text{melt}} = \frac{W_{\text{Sn}}}{W_{\text{melt}}} [m]_{\text{Sn}} \quad (1)$$

where m represents individual light metals including aluminum, sodium, and lithium dissolved in the cryolitic melt that have been stripped into the Sn phase. $[m]_{\text{melt}}$ is the individual solubility of m in the cryolitic melt, W_{Sn} the weight of tin alloy recovered, W_{melt} the weight of cryolitic sample transferred to compartment B, and $[m]_{\text{Sn}}$ the concentration of metal m in the tin phase obtained by chemical analysis.

The total solubility which is the summation of individual solubilities of metals, was calculated according to:

$$C_t (\text{Al wt}\%) = [\text{Al}]_{\text{melt}} + \frac{26.98}{3 \times 22.99} [\text{Na}]_{\text{melt}} + \frac{26.98}{3 \times 6.94} [\text{Li}]_{\text{melt}} \quad (2)$$

where C_t represents the total solubility in units of apparent Al wt%, $[\text{Al}]_{\text{melt}}$ the metallic aluminum solubility in Al wt%, $[\text{Na}]_{\text{melt}}$ the metallic sodium solubility in Na wt%, and $[\text{Li}]_{\text{melt}}$ the metallic lithium solubility in Li wt%, calculated according to equation (1).

1. Dissolved Metals in Cryolitic Melts with Varying Cryolite Ratio

The effect of cryolite ratio on the dissolved metals was studied in a range of cryolite molar ratio from 1.5 to 4.2 with constant concentrations of 1.0 wt% LiF and 5.0 wt% Al_2O_3 at 995°C. The total metallic solubility and individual metallic solubilities are presented separately as follows.

Individual Solubilities of Light Metals

The metallic solubilities of individual aluminum, sodium, and lithium when varying cryolite ratio are shown in Figure 3. Because of the far different magnitudes of these three metallic solubilities, they are presented in a semi-logarithmic domain for an easy comparison. The solubility of the individual metals is also referred to as the "true solubility of the metal" in this study.

The individual solubilities of metallic sodium and aluminum varied oppositely when the cryolite ratio increased. As the cryolite molar ratio increased from 1.6 to 4, the true solubility of metallic sodium increased from about 0.025 to 0.45 wt% Na while the true solubility of aluminum decreased from about 0.025 to 0.0032 wt% Al. In other words, the ratio of true solubilities of metallic sodium to metallic aluminum, $[\text{wt}\% \text{Na}]/[\text{wt}\% \text{Al}]$, increased from around 1 to over 100. At CR=2.5, the concentration of the dissolved sodium (in wt% Na) was about 10 times greater than that of dissolved aluminum (in wt% Al).

Our results, shown in Figure 3, are different from those reported by Yoshida, et al.,^[11] Thonstad,^[12] and Haupin.^[8] Yoshida, et al., used a technique of reacting frozen bath sample in boiling distilled water and then titrating the solution with HCl to reveal the free sodium content. They found the sodium content nonlinearly increased with the increasing cryolite ratio, but no information on aluminum solubility was reported.

Thonstad used alcohol to react with the sodium content followed by the addition of HCl for aluminum analysis. Both aluminum and sodium were detected, but the sodium contents as reported were lower than the results of this study. These investigators attempted to separate the dissolved aluminum and sodium by using different reactants in gas volumetric or titration analysis so that individual metallic solubilities could be determined during analyzing their quenched cryolitic samples. These accountabilities ended up with results of either all aluminum or all sodium dissolved in the cryolitic melts. Therefore, no great reliance can be placed in the reported methods of separately analyzing for aluminum and sodium.

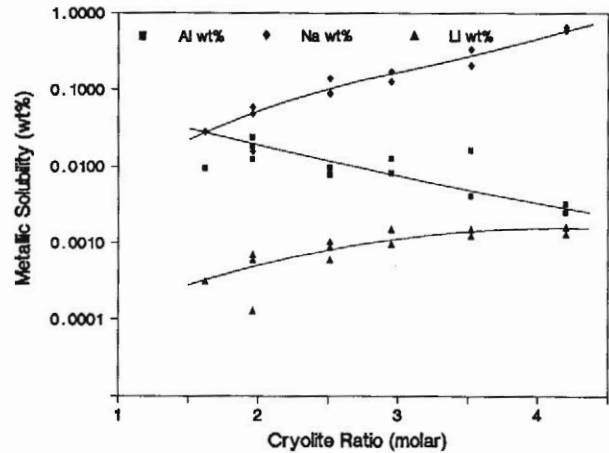
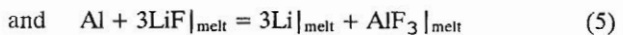
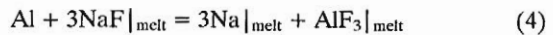


Figure 3: Individual solubilities of metals in the cryolitic melts at 995°C: 5.0 wt% Al_2O_3 and 1.0 wt% LiF (synthetic).

The dissolved lithium in the cryolitic melts was also detected by chemical analysis of the recovered tin phase. Figure 3 shows that the concentration of metallic lithium increased with increasing cryolite ratio even though the concentration of LiF was kept constant at 1.0 wt% for all of the tests. The greatest concentration of dissolved lithium measured was below 20 ppm (or 0.002 wt% Li). Metallic lithium was of the same magnitude as the metallic aluminum when the cryolite molar ratio was greater than 3.5.

The individual solubilities of aluminum, sodium, and lithium in the cryolitic melts can be explained by thermodynamic analysis. Under conditions of thermodynamic equilibrium between the cryolitic melt and the aluminum metal phase, exchange reactions can occur. These reactions include:



These reactions can occur either at the interface of the melt and aluminum phase or in the melts where metallic aluminum has a unity activity as expressed by reaction (3). The magnitudes of all dissolved species aluminum, sodium, and lithium depend on the electrolyte temperature and composition as expressed by reaction (4) and (5). At a fixed temperature, as the cryolite ratio increases, the concentration or activity of NaF correspondingly increases while that of AlF_3 decreases, which according to reaction (4) and Le Chatelier-Braun principle, would result in greater metallic sodium activity and concentration. On the other hand, a lower concentration or activity of AlF_3 as the cryolite ratio increases would increase the metallic lithium solubility when the concentration or activity of LiF is held constant.

Total Metallic Solubility

The total metallic solubility as a function of cryolite ratio, CR, is shown in Figure 4. Some literature data are also presented. The concentration of dissolved species, which is a summation of individual solubilities of aluminum, sodium, and lithium in the cryolitic melts, increased non-linearly with increasing cryolite ratio. Because of different experimental conditions, the results obtained in this investigation should not be compared directly with those reported in the literature shown in Figure 4. Nevertheless, some similarities of our results to the reported data are still observed in Figure 4. The total metallic solubility results lay between those reported by Thonstad^[11] and Yoshida and Dewing^[4] in the cryolite ratio range from 2 to 3.5. Beyond CR=3.5, the total solubility was much greater than those previously reported.

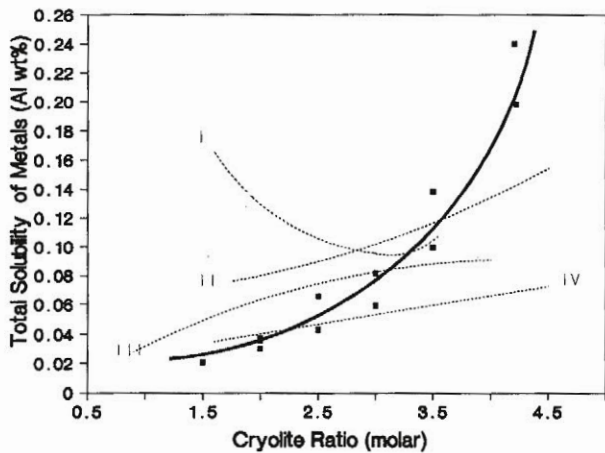


Figure 4: Metallic solubility (wt% Al) as a function of the molar cryolite ratio: ■: present investigation--5.0 wt% Al₂O₃ and 1.0 wt% LiF at 995°C:
 I. Vetyukov and Vinokurov,^[2] 1.5% alumina at 1000°C;
 II. Thonstad,^[12] alumina-saturated at 1000°C;
 III. Odegard,^[7] alumina-saturated at 1000°C; and
 IV. Yoshida and Dewing,^[4] alumina-saturated at 1000°C.

The elevated solubility values beyond CR=3.5 using our technique are believed to be reasonable. The particular experimental technique can not only provide us with the individual metallic solubilities in the cryolitic melts as already described, but also represents the real equilibrium state under which the metallic species are dissolved in the melts. Besides enabling us to obtain very accurate analysis results from recovered tin alloys, this technique also eliminates the processes involved in the conventional methods such as hydrogen volumetric analysis for metal solubility.

The processes in the volumetric determination of metal solubility include cryolite sample quenching and grinding. That complex analyzing process may have some unnecessary exposure of cryolitic samples to air or an environment which may contain even very low O₂ or H₂O. It has been shown in Figure 3 that for the cryolite CR greater than 2.5, the dissolved metallic species are dominated by metallic sodium.

When using the hydrogen volumetric analysis technique, the metallic sodium dissolved in the cryolitic melts may be easily lost if very special measures to exclude moisture during the handling of the cryolitic samples are not taken. Some detailed discussions and comments have already been provided by

Odegard^[13] and Grjotheim, et al.,^[14] on experimental techniques, test procedures, and the total solubility in cryolitic melts.

The use of our experimental technique minimizes sodium losses. Given the reproducibility and the conservation of sodium in our method, we find no reason to suspect the high solubility values at high cryolite ratios.

2. Dissolved Metals in Cryolitic Melts with Varying Al₂O₃ Concentration

The effect of Al₂O₃ concentration variation on the metallic solubility was examined in melts with CR=2.5 and 3.0 at 995°C. LiF concentration was held constant at 1.0 wt%.

Individual Solubilities of Light Metals

Individual solubilities of light metals in the two melts of selected cryolite ratios are presented respectively in Figure 5 (a) and (b). Semi-logarithm domain was used again for comparing the three metallic species dissolved in the melts. The true solubility of metallic aluminum increased slightly with increasing Al₂O₃ concentration.

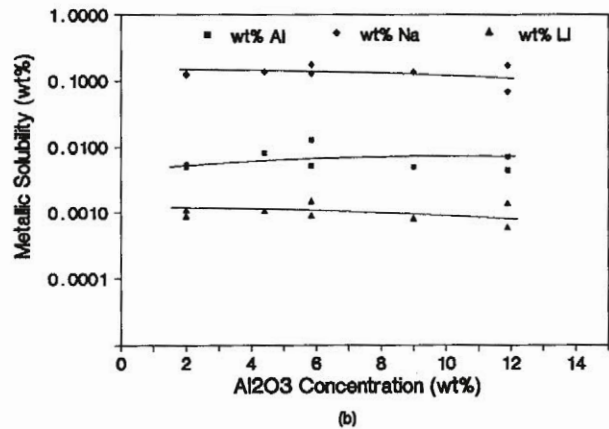
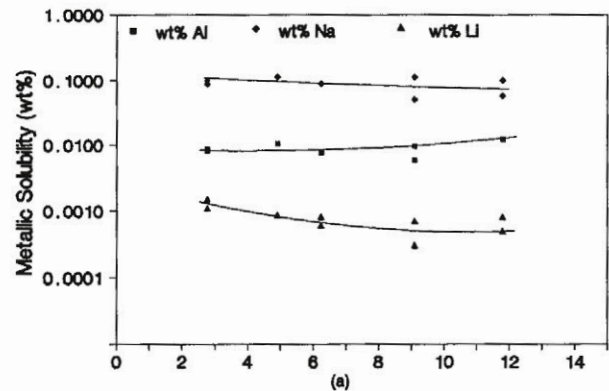


Figure 5: Individual solubilities of metals in the cryolitic melts as a function of Al₂O₃ concentration at 995°C: (a) CR=2.5 and (b) CR=3.0. 1.0 wt% LiF.

At present, we do not have an unequivocal rationale for the true aluminum solubility increase with increasing Al₂O₃ concentration. It may be related to changes in the ionic structure of the melts when the Al₂O₃ content is increased. Kvande^[15] has proposed that the structure of Al₂O₃ dissolved in

the cryolitic melts changes with Al_2O_3 content. The aluminum oxyfluoride complexes seem to have a positive effect on the dissolved aluminum when the Al_2O_3 increases. It is interesting to note that ratio of the metallic solubility, $[Al]_{melt}$, to the ionic Al component present in the melt was independent of the increasing Al_2O_3 concentration.

Figure 5 also shows that concentrations of both metallic sodium and lithium decreased when increasing Al_2O_3 concentration.

When Al_2O_3 concentration increases, the molar fraction of NaF, N_{NaF} , correspondingly decreases for a fixed CR. If examining the ratio of the sodium solubility, $[Na]_{melt}$, to the molar fraction of NaF, N_{NaF} , for both CR=2.5 and CR=3.0, one would find that the ratio does not vary with the change of Al_2O_3 concentration. A lack of change in the ratio during an addition of the Al_2O_3 to the melt can be attributed to a dilution effect on the metallic sodium solubility, $[Na]_{melt}$.

Al_2O_3 also affected the metallic lithium solubility behavior in the cryolitic melts even though the melts contained only 1.0 wt% LiF. Addition of Al_2O_3 decreases the lithium solubility. For the whole Al_2O_3 concentration range studied, metallic sodium dominated all dissolved metallic species, and its solubility (in wt% Na) was over 10 times greater than that of aluminum (in wt% Al) and about 100 times greater than that of lithium (in wt% Li) in the melts with CR=2.5. No changes in the trends of true solubilities of these three metals were observed for the melts with CR=3.0 except that the magnitude of sodium solubility was greater and aluminum solubility lower than for the CR=2.5 melts.

Total Metallic Solubility

The total solubility variation with Al_2O_3 concentration (including previously-published data) is plotted in Figure 6.

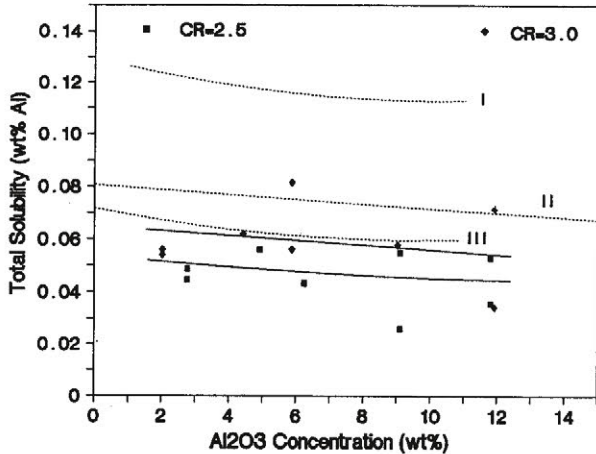


Figure 6: Total metal solubility as a function of Al_2O_3 concentration: solid lines: this study--1.0 wt% LiF at 995°C:
 I. Vetyukov, et al.,^[16] CR=3.20 at 1060°C;
 II. Arthur,^[17] CR=3.0 at 1020°C; and
 III. Odegard,^[7] CR=2.25 at 1000°C.

The greatest values of the total metal solubility were given by Vetyukov, et al.,^[16] because their tests were conducted under experimental conditions with the greatest cryolite ratio (CR=3.20) and greatest bath temperature (1060°C). Figure 6 shows that our experimental tests for alumina concentration had some variability on replicate tests for the melts with both CR=2.5 and CR=3.0. The reason for this is not understood at this time. However, the general trend of decreasing total metal solubility with increasing Al_2O_3 concentration agreed well with

prior work. In all cases, the slope of the variations in solubility with increasing Al_2O_3 concentration was very small.

Our tests were carried out in the cryolitic melts containing 1.0 wt% LiF at 995°C. The tests reported in the literature were carried out at greater temperatures (1000°C, 1020°C, and 1060°C); consequently, our values of total solubility are lower than those previously-reported values (see Figure 6). Metallic solubility decreased from 0.061 to 0.054 wt% Al for CR=3.0 melts and from 0.051 to 0.044 wt% Al for CR=2.5 melts when the Al_2O_3 concentration was increased from around 2 wt% to alumina saturation. About 13 to 16% of decrease in total solubility was obtained for the whole Al_2O_3 range studied.

3. Dissolved Metals in Cryolitic Melts with Varying Temperature

Temperature effects on the metallic solubility were measured in the cryolite CR=2.5 and CR=3.0 melts containing constant 5.0 wt% Al_2O_3 and 1.0 wt% LiF.

Individual Solubilities of Light Metals

The concentrations of metallic species aluminum, sodium, and lithium dissolved in the cryolitic melts versus temperature are plotted in Figure 7 (a) and (b). The solubility of each metal increased with increasing temperature. In the semi-logarithmic domain, the concentrations of these three metallic species in

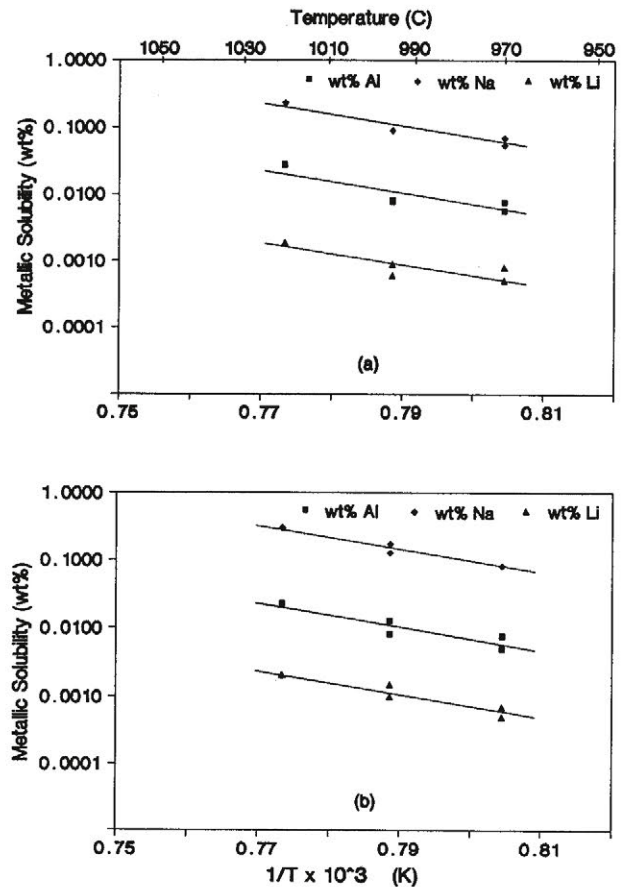


Figure 7: Individual solubilities of metals in the cryolitic melts as a function of temperature: (a) CR=2.5 and (b) CR=3.0. 5.0 wt% Al_2O_3 and 1.0 wt% LiF.

both CR=2.5 and CR=3.0 melts vary linearly with the reciprocal of electrolyte temperature.

As shown in Figure 7 (a), for the melt with CR=2.5, the magnitude of dissolved sodium was around 0.1 wt% Na, dissolved aluminum, 0.01 wt% Al, and dissolved lithium, 0.001 wt% Li at 1000°C. Metallic sodium is the dominant component of the total solubility in the cryolitic melt at all temperatures. The ratios of the three metallic species, [Na]/[Al], [Na]/[Li], remained constant over the temperature range.

The linear relationships of the individual metallic solubilities with the inverse of the absolute temperature follow equations derived from thermodynamic analysis.^[18] For the true aluminum solubility according to reaction (3), the following relationship with temperature can be derived:

$$\log[Al]_{\text{melt}} = -\frac{A}{2.303RT} - \frac{B}{2.303R} \quad (6)$$

where R is gas constant, T the temperature in Kelvin, and constant A and B are the coefficients for the excess free energy of aluminum dissolving in the cryolitic melts, $\Delta G_{Al,\text{melt}}^{\text{xs}}$:

$$\Delta G_{Al,\text{melt}}^{\text{xs}} = A + BT \quad (7)$$

For the individual solubilities of metallic sodium and lithium according to exchange reaction (4) and (5), the relationships with temperature follow equation:

$$\log[m]_{\text{melt}} = -\left(\frac{3A + \Delta H_{i,T}}{3 * 2.303R}\right) \cdot \frac{1}{T} + C_i \quad (8)$$

where m represents metallic Na or Li, ΔH_i the heat of reaction (4) or (5), and C_i a constant.

Total Metallic Solubility

Total metallic solubility versus melt temperature is plotted in Figure 8. Literature data from several sources is also

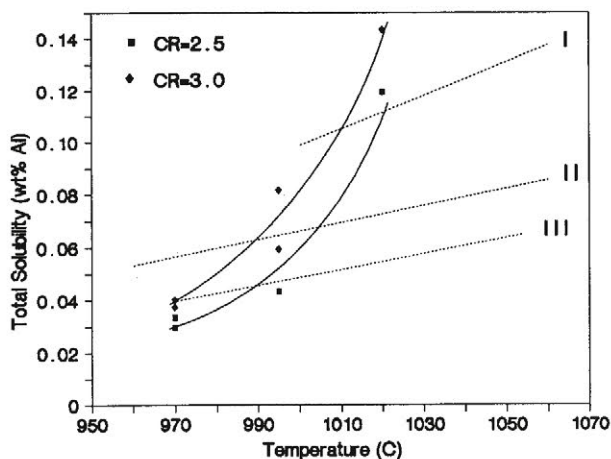


Figure 8: Total metallic solubility as a function of temperature: solid lines: this study--5.0 wt% Al₂O₃ and 1.0 wt% LiF;
 I. Thonstad,^[12] CR=3.0 melts saturated with alumina;
 II. Odegard,^[7] CR=2.25 melts saturated with alumina; and
 III. Yoshida and Dewing,^[4] CR=3.0 melts saturated with alumina.

presented. Metallic solubility increased with increasing temperature. In contrast to the reported data which shows a linear relationship between solubility and temperature, an exponential type of relationship was observed for the experimental results in this investigation. The total solubility of this study was more dependent upon temperature than those reported in the literature. When temperature was increased from 970 to 1020°C, the total solubility increased from 0.04 to over 0.14 wt% Al in the CR=3.0 melt and from 0.03 to 0.12 wt% Al in the CR=2.5 melt. Both cryolitic melts contained 5.0 wt% Al₂O₃ and 1.0 wt% LiF.

The exponential behavior of the total solubility variation with temperature was verified from the thermodynamic analysis presented in the previous section. A possible explanation for the low solubilities at high temperatures as reported in the literature, is that the dissolved metals are dominated by metallic sodium species which are very reactive. In some of the reported experimental tests, either the open test atmosphere or graphite crucible employed could act as "sinks" and result in an unsaturated cryolitic melt. Additionally, quenching and handling of samples before the hydrogen volumetric analysis may lead to exposure of the samples to air or atmospheres containing even very low concentration of O₂ or H₂O, which all could result in significant losses of dissolved metallic sodium content.

4. Dissolved Metals in Cryolitic Melt with Varying LiF Concentration

Metallic solubility variation as a function of LiF concentration was studied in the CR=2.5 and CR=3.0 melts containing 5.0 wt% Al₂O₃ at 995°C. LiF concentration was intentionally increased up to 10 wt% in order to examine the metallic lithium content dissolved in the cryolitic melts.

Individual Solubilities of Light Metals

The individual solubilities of metallic aluminum, sodium, and lithium versus LiF concentration are plotted in Figure 9 (a) and (b). The solubilities of both metallic aluminum and sodium decreased with increasing LiF concentration. This effect is responsible for the total solubility decrease. Higher LiF concentration resulted in greater metallic lithium content in the melts. For the CR=2.5 melt containing 8.7 wt% LiF, the metallic lithium content could be as high as 34 ppm.

Figure 9 (a) and (b) also show that the solubility of metallic lithium (in wt% Li) was close to that of metallic aluminum (in wt% Al) when LiF concentration was greater than 8 wt%. However, both aluminum and lithium were still minor species dissolved in the melts when compared with sodium. The dominant role of metallic sodium could not be surpassed by metallic lithium even though the LiF concentration was increased up to 10 wt% (18 mole%).

Again, since the dissolved metallic species are controlled by reactions (3) to (5), the magnitudes of the solubilities in the melts are expected to change with the electrolyte composition when varying LiF concentration. As LiF concentration increases, the concentrations or activity of both AlF₃ and NaF decreases, which is unfavorable to both metallic aluminum and sodium formation and dissolution in the melts according to reactions (3) and (4). On the other hand, greater concentration or activity of LiF could mean an increase of the metallic Li solubility because of increase in both reactivity of aluminum with LiF according to reaction (5) and compatibility of lithium with the cryolitic melts.

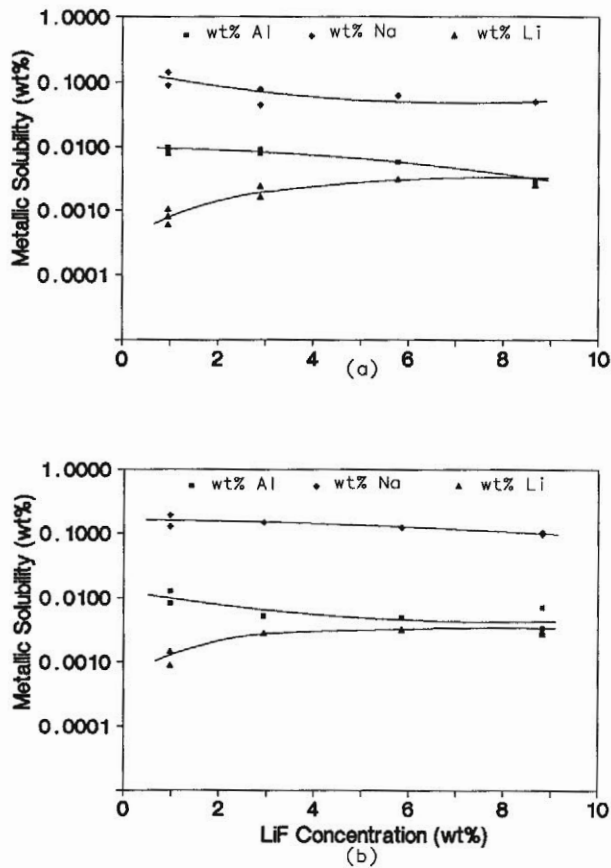


Figure 9: Individual solubilities of metals in the cryolitic melts as a function of LiF concentration at 995°C: (a) CR=2.5 and (b) CR=3.0. 5.0 wt% Al₂O₃.

Total Metallic Solubility

The total metallic solubility variation with increasing LiF concentration is shown in Figure 10. The total solubility decreased with increasing LiF concentration. For the CR=3.0 melts, the solubility decreased from 0.08 to 0.05 wt% Al when the LiF concentration was increased from 1 to 9 wt%. In other words, every increase of 1.0 wt% LiF resulted in a decrease of the total solubility by about 0.004 wt% Al at constant 995°C. The same trend for total solubility variation in the CR=2.5 melts was also observed when the LiF concentration was increased.

Summary of Discussion

Our results and discussion show that the dissolved metals in the cryolitic melts consist of metallic aluminum, sodium, and lithium. The magnitudes of these individual metallic solubilities are dependent on the cryolitic electrolyte composition and temperature. Metallic sodium dominates all of the species dissolved in the cryolitic melts. Decreasing cryolite ratio (increasing excess AlF₃) and temperature and increasing additive LiF concentration can decrease the metallic sodium magnitude, which will result in lower total metal solubility in the melts. The theoretical significance of these results lies in a proper understanding of the thermodynamics of the cryolite-dissolved metals system. A better understanding would then help to characterize and formulate metal dissolution and oxidation mechanisms. From a practical standpoint, the results and metal dissolution mechanism characterization may provide a means to optimize bath chemistry for improving the current

efficiency of Hall cells in aluminum production, as will be shown in the accompanying paper.^[19]

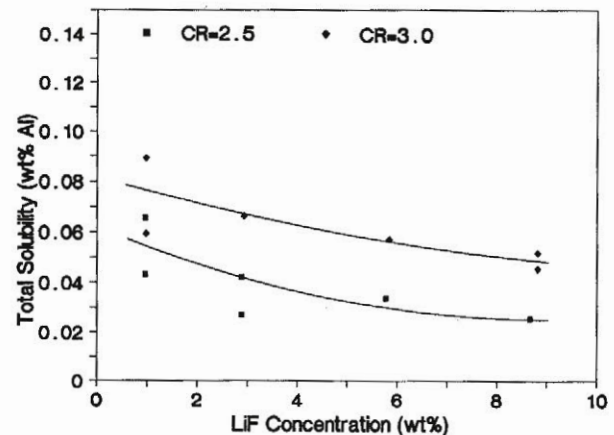


Figure 10: Total metallic solubility in the cryolitic melts as a function of LiF concentration at 995°C: 5.0 wt% Al₂O₃.

Conclusions

Although intensive research has been carried out for measurement of the dissolved metals in cryolitic melts, little work has been reported on the experimental determination of solubilities of individual metals such as aluminum, sodium, and lithium. This paper presents the first reported experiments using the tin extraction-stripping technique on the identification and determination of the those metals dissolved in the cryolitic melts in equilibrium with aluminum phase. The following conclusions have been obtained:

1. In cryolitic melts containing LiF as an additive, the total metallic solubility consists of aluminum, sodium, and lithium.
2. Total metallic solubility as measured by using the Sn extraction-stripping technique is in fair agreement with those reported in the literature. The total solubility increases from about 0.02 wt% Al to over 0.2 wt% Al when cryolite molar ratio varies from 1.6 to 4.0 at 995°C.
3. Solubility of metallic aluminum decreases while that of metallic sodium increases with increasing cryolite ratio. The solubility ratio of metallic sodium to aluminum increases with increasing cryolite ratio.
4. Increasing Al₂O₃ depresses the solubilities of metallic sodium and lithium, but increases the solubility of metallic aluminum. Addition of LiF depresses the solubilities of aluminum and sodium, but increases the solubility of metallic lithium.
5. Metallic lithium dissolves in the cryolitic melts even when the melts contain as low as 1.0 wt% LiF. However, lithium's solubility is a minor component of the total solubility even when the LiF concentration is increased up to 10 wt%.
6. Metallic sodium is dominant among the metallic species dissolved in the cryolitic melts. For the melts with cryolite molar ratio greater than 2.5, the solubility of metallic sodium is far higher than that of metallic aluminum and lithium. The belief of dissolved metals as only aluminum when describing metal dissolution processes should be revised.

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