RAPID PUBLICATION

Chemical Interactions of Dross with Water and Water Vapor in Aluminum Scrap Remelting

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Remelting of Aluminum alloys such as Used Beverage Container (UBC) is done under a cover of molten salt flux based on NaCl-KCl. After the remelting process is over, the used flux (called dross) reacts with water vapor to produce gaseous emissions. Dross is also leached by dissolving in water and subsequently crystallized to regenerate the salt flux for reuse. This leaching process also generates emissions. The calculations indicate that the trace components, such as AlN and Al\textsubscript{4}C\textsubscript{3} present in the dross react with water (or water vapor) to produce NH\textsubscript{3} (g) and CH\textsubscript{4} (g) in quantities greater than HCl (g) or HF (g) generated from reactions of NaCl, KCl, and NaF with water or water vapor.

(Received August 26, 1996)

Keywords: aluminum recycling, remelting, dross, thermodynamic calculations, chemical interactions

I. Introduction

Remelting of Al, Al-alloys, and Used Beverage Container (UBC) is carried out under a cover of molten salt flux to prevent oxidation of the alloys and also to improve the coalescence of molten metal. The salt fluxes are generally based on equimolar NaCl-KCl compositions with fluoride additions, such as NaF, Na\textsubscript{3}AlF\textsubscript{6}, or KF of up to 10% to improve the coalescence and hence, the remelting process. After the aluminum metal has been melted, the used flux (called dross) reacts with water vapor (moisture) present in air and generates gaseous emissions. Also, the dross is usually leached by water to dissolve the water soluble compounds. The solution is then dried to recrystallize the salt fluxes for reusing them in aluminum recycling process. It is estimated that each metric ton of dross produces twelve cubic meters of gaseous emissions\textsuperscript{(1)}, some of which are explosive, poisonous and/or have very unpleasant odor. This paper describes thermodynamic calculations made for these systems which have helped make quantitative predictions of the extent of emissions.

II. Dross and Reactions with Water/Water Vapor

As mentioned before, the major components of the salt fluxes are NaCl, KCl, and fluorides (NaF, Na\textsubscript{3}AlF\textsubscript{6}, or KF). However, the dross also contains minor amounts of components like AlN and Al\textsubscript{4}C\textsubscript{3}. A typical analysis of dross roller fines is shown in Table 1\textsuperscript{(2)}. Other investigators have also reported the presence of trace components AlN, Al\textsubscript{4}C\textsubscript{3}\textsuperscript{(3)}, Al\textsubscript{2}S\textsubscript{3}\textsuperscript{(4)}, and AlF\textsubscript{3}\textsuperscript{(5)}. The reactions that take place during the water leaching of dross are as follows (all equilibrium constants are at 298 K, and are taken from reference\textsuperscript{(5)}):

\[ \text{NaCl} + \text{H}_2\text{O} (l) = \text{NaOH} + \text{HCl} (g) \]
\[ K = 2.48 \times 10^{-26} \]  

\[ \text{KCl} + \text{H}_2\text{O} (l) = \text{KOH} + \text{HCl} (g) \]
\[ K = 8.1 \times 10^{-31} \]  

\[ \text{NaF} + \text{H}_2\text{O} (l) = \text{NaOH} + \text{HF} (g) \]
\[ K = 4 \times 10^{-23} \]  

\[ 2\text{AlN} + 3\text{H}_2\text{O} (l) = \text{Al}_2\text{O}_3 + 2\text{NH}_3 (g) \]
\[ K = 4.88 \times 10^{77} \]  

\[ 2\text{AlN} + 6\text{H}_2\text{O} (l) = 2\text{Al(OH)}_3 + 2\text{NH}_3 (g) \]
\[ K = 8.11 \times 10^{84} \]  

\[ \text{Al}_4\text{C}_3 + 6\text{H}_2\text{O} (l) = 2\text{Al}_2\text{O}_3 + 3\text{CH}_4 (g) \]
\[ K = 1.87 \times 10^{97} \]

Table 1 Chemical analysis of dross\textsuperscript{(2)}.

<table>
<thead>
<tr>
<th>Compound/Action</th>
<th>mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>4.21</td>
</tr>
<tr>
<td>C</td>
<td>0.58</td>
</tr>
<tr>
<td>Cryolite (Na\textsubscript{3}AlF\textsubscript{6})</td>
<td>4.49</td>
</tr>
<tr>
<td>Alumina (Al\textsubscript{2}O\textsubscript{3})</td>
<td>23.01</td>
</tr>
<tr>
<td>Al metal</td>
<td>2.12</td>
</tr>
<tr>
<td>AlN</td>
<td>2.94</td>
</tr>
<tr>
<td>Al\textsubscript{4}C\textsubscript{3}</td>
<td>0.24</td>
</tr>
<tr>
<td>NaCl</td>
<td>37.88</td>
</tr>
<tr>
<td>KCl</td>
<td>23.26</td>
</tr>
<tr>
<td>Loss on Ignition</td>
<td>0.68</td>
</tr>
</tbody>
</table>
\[
\text{Al}_2\text{C}_3 + 12\text{H}_2\text{O} (l) \rightarrow 4\text{Al(OH)}_3 + 3\text{CH}_4 (g)
\]
\[K = 5.18 \times 10^{291}\] (7)

Gaseous emissions can also result from reactions between the salt flux and \(\text{H}_2\text{O} (g)\) similar to those shown above, in which \(\text{H}_2\text{O} (g)\) reacts with salt flux components instead of \(\text{H}_2\text{O} (l)\). The standard Gibbs Energies \((\Delta G^o)^s\) for these reactions as a function of temperature are shown in Fig. 1.

### III. Thermodynamic Modeling

To estimate the extent of gaseous emissions from thermodynamic considerations, equilibrium composition calculations for these systems were performed using a commercially available software package, HSC CHEMISTRY\(^{(9)}\). This thermodynamic calculation program minimizes the total Gibbs Free Energy, \(G\), by a method similar to the well known SOLGASMIX computer code\(^{(8)}\).

Before the calculations can be carried out, the relevant species to be included in the calculations have to be identified. The total number of species possible for this complex system is 312 (from the database of HSC CHEMISTRY), all of which cannot be included because of the restrictions imposed in the software. The software allows a maximum of 150 species in the calculations. To identify the predominant species, preliminary calculations were made involving the reactants and all possible product species (in separate calculations with 150 species in each calculation). On the basis of these calculations, the dominant species were identified (based on the equilibrium amounts) to be included in the final calculations. Gaseous, liquid and solid species were considered in these calculations. The species which could be considered as predominant numbered 30 and are listed in Table 2.

### Parameters for the calculations

The amounts of the constituents in the flux and other relevant parameters are given in Table 3. The parameters and amounts are based on typical laboratory scale experiments. However, calculations were also done for fluxes in large quantities which represent typical industrial conditions, and are described in a later section. Since the objective was to estimate the amount of gaseous emissions from room temperature (reaction with water) to higher temperature (reaction with water vapor), the calculations were performed in a range from 298 K \((25^\circ\text{C})\) to 973 K \((700^\circ\text{C})\).

### IV. Results and Discussion

Figure 2(a) shows the variation of the equilibrium amounts of the gaseous emissions, \(\text{NH}_3\), \(\text{CH}_4\), \(\text{HCl}\), and \(\text{HF}\), as a function of the amount of water vapor at 673 K \((400^\circ\text{C})\). It is seen that the predicted amounts of \(\text{NH}_3\) and \(\text{CH}_4\) are many orders of magnitude greater than those of \(\text{HCl} (g)\) or \(\text{HF} (g)\) despite the fact that only minor amounts (0.24% \(\text{Al}_2\text{C}_3\) and 2.94% \(\text{AlN}\)) of \(\text{Al}_2\text{C}_3\) and \(\text{AlN}\) are present. The calculated results for room temperature (298 K) are shown in Fig. 2(b) which show a similar trend.

Figure 3 shows the variation of the calculated amounts of gases as a function of temperature. The amount of \(\text{H}_2\text{O} (g)\) in the system is 0.5 moles with the amount of flux components being the same as described in Table 3. Figure 3 shows that the amounts of \(\text{NH}_3 (g)\) and \(\text{CH}_4 (g)\) are predicted to decrease as the temperature increases while those of \(\text{HCl} (g)\) and \(\text{HF} (g)\) are predicted to increase with increase in temperature. This is due to the fact that the equilibrium constants for the reactions of \(\text{AlN}\) and \(\text{Al}_2\text{O}_3\) with \(\text{H}_2\text{O} (g)\) decrease as a function of temperature while those of \(\text{NaCl}\) and \(\text{NaF}\) with \(\text{H}_2\text{O} (g)\) increase as the temperature increases, as can be concluded from Fig. 1. It can also be noted that the \(\Delta G^o\)'s for the reactions of \(\text{AlN}\), \(\text{AlP}\), \(\text{Al}_2\text{S}_3\), and \(\text{Al}_2\text{O}_3\) with \(\text{H}_2\text{O} (l, g)\) are large negative numbers (i.e. large equilibrium con-

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### Table 2. Species considered in the thermodynamic calculations.

<table>
<thead>
<tr>
<th>(\text{Species} (g))</th>
<th>(\text{Reactant} (l))</th>
<th>(\text{Product} (l))</th>
<th>(\text{Product} (g))</th>
<th>(\text{Product} (s))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2) (g)</td>
<td>(\text{Al(OH)}_3)</td>
<td>(\text{NH}_3\text{OH})</td>
<td>(\text{C} (\text{Diamond}))</td>
<td>(\text{NaF})</td>
</tr>
<tr>
<td>(\text{H}_2\text{O} (g))</td>
<td>(\text{Al}_2\text{O}_3\cdot\text{H}_2\text{O})</td>
<td>(\text{Al})</td>
<td>(\text{Al}_2\text{O}_3) (Corundum)</td>
<td>(\text{AlN})</td>
</tr>
<tr>
<td>(\text{N}_2 (g))</td>
<td>(\text{Al}_2\text{O}_3\cdot3\text{H}_2\text{O})</td>
<td>(\text{Al}_2\text{O}_3) (Gamma)</td>
<td>(\text{HF} (g))</td>
<td>(\text{KOH})</td>
</tr>
<tr>
<td>(\text{CH}_4 (g))</td>
<td>(\text{AlO-OH})</td>
<td>(\text{Al}_2\text{O}_3) (Delta)</td>
<td>(\text{Al}_2\text{O}_3) (Kappa)</td>
<td>(\text{HCl} (g))</td>
</tr>
<tr>
<td>(\text{Al}_2\text{O}_3)</td>
<td>(\text{H}_2\text{O})</td>
<td>(\text{Al}_2\text{O}_3) (Kappa)</td>
<td>(\text{NaOH})</td>
<td>(\text{KF})</td>
</tr>
</tbody>
</table>
Table 3  Amounts of various flux constituents used in the calculations (for all calculations except those corresponding to Fig. 4).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>5 moles</td>
</tr>
<tr>
<td>KCl</td>
<td>5 moles</td>
</tr>
<tr>
<td>NaF</td>
<td>1 mole</td>
</tr>
<tr>
<td>AlN</td>
<td>0.3 moles</td>
</tr>
<tr>
<td>Al₂C₃</td>
<td>(0.1-2) moles</td>
</tr>
<tr>
<td>H₂O (l, g)</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>298 K–973 K</td>
</tr>
</tbody>
</table>

Fig. 2  (a) Variation of the equilibrium amounts of gaseous species NH₃, CH₄, HCl, and HF as a function of amount of H₂O (g) in the system at 673 K. (b) Variation of the equilibrium amounts of gaseous species NH₃, CH₄, HCl, and HF as a function of amount of H₂O (g) in the system at 298 K.

Fig. 3  Variation of the equilibrium amounts of gaseous species as a function of temperature.

Fig. 4  Variation of the equilibrium amounts of gaseous species as a function of flux mass at 298 K.

In order to estimate the amounts of the gaseous emissions when larger amounts of salt flux react with H₂O (g), calculations were also done with varying amounts of salt flux. Figure 4 shows the results of the calculations done with varying amounts of the salt flux at 298 K (25°C). The amounts of each of the constituents of flux and H₂O were scaled up by factors of 10, 20, 100 and 200 compared to the parameters shown in Table 3. In each case, it is seen that the amount of predicted emissions is also scaled up by the same factor, as one would expect based on thermodynamic considerations. Calculations were
also done at other temperatures in the range from 298 to 973 K and a similar trend was observed. These results should be useful in estimating the emissions when reactions of larger quantities of salt fluxes with water or water vapor have to be considered. From the results in Fig. 2(b), the proportion of NH\(_3\) (g)/CH\(_4\) (g) can be calculated as 1.84 at 298 K. This prediction is in fairly good accord with the ratio of 1.4 calculated from the measured values of Unger and Beckman\(^{(3)}\), shown in Table 4. A more direct comparison of the calculated and experimental values could not be made because the amounts of fluxes and water used for the reactions are not reported in the paper. It should be emphasized that these results are based on thermodynamic calculations and do not take kinetics into account. Hence these results would be applicable to situations where thermodynamic equilibrium has been established.

It was mentioned earlier in one case\(^{(3)}\), Al\(_2\)S\(_3\) and AlP have been found to be trace constituents in addition to the more common minor components AlN and Al\(_2\)C\(_3\). Although Al\(_2\)S\(_3\) and AlP have not been taken into account in these calculations, some predictions can be made regarding the amounts of H\(_2\)S (g) and PH\(_3\) (g) which could be expected. The relevant reactions are (equilibrium constants at 298 K (25°C) from reference\(^{(5)}\)):

\[
\begin{align*}
\text{Al}_2\text{S}_3 + 3\text{H}_2\text{O} (l) & = \text{Al}_2\text{O}_3 + 3\text{H}_2\text{S} (g) \\
K &= 1.11 \times 10^{45} \\
2\text{AlP} + 3\text{H}_2\text{O} (l) & = \text{Al}_2\text{O}_3 + 2\text{PH}_3 (g) \\
K &= 2.79 \times 10^{92}
\end{align*}
\]

The variations of the standard Gibbs Energies (\(\Delta G^0\)'s) for the above reactions as a function of temperature are shown in Fig. 1. It can be deduced that the equilibrium constants decrease as the temperature increases. Also, the equilibrium constants are much larger compared to those of reactions of NaCl and KCl with H\(_2\)O (eq. (1) and eq. (2)). Based on this information and the results obtained with Al\(_2\)C\(_3\), it is possible to conclude that H\(_2\)S and PH\(_3\) emissions should also be expected to be more significant compared to HCl (g) or HF (g). This is also in agreement with the measured values of the gaseous emissions by Unger and Beckman, shown in Table 4, which shows a very small amount of PH\(_3\) and a comparatively more significant amount of H\(_2\)S.

V. Summary and Conclusions

Equilibrium composition calculations have been done in the salt flux/(water, water vapor) systems to estimate the amounts of gaseous emissions generated due to the reactions. The results indicate that the majority of the emissions is due to reactions of minor components like AlN and Al\(_2\)C\(_3\) in the salt flux with water/water vapor. The resulting emissions are thus predominantly Ammonia and Methane rather than HCl or HF.

Acknowledgment

The authors would like to acknowledge the financial support for this research from the U.S. Bureau of Mines through the Generic Mineral Technology Center for Pyrometallurgy at the University of Missouri-Rolla.

REFERENCES

5. HSC CHEMISTRY, version 2.0, Outokumpu Research Oy, Pori, Finland.