Oxidation-Reduction Equilibrium of Cu²⁺/Cu⁺ in Binary Alkaline Sulfate Melts

T. YAMAMOTO, N. YAMANO-UCHI, K. MASAMURA, M. TAMURA, and M. IWASE

Oxidation-reduction equilibria for a Cu²⁺/Cu⁺ couple in binary alkaline sulfate melts, Li₂SO₄ + R₂SO₄ (R = Na, K, Rb, Cs), were determined at temperatures of 973, 1023, and 1073 K by equilibrating these melts with gas mixtures of Ar + O₂ + SO₂. RedOx equilibria are well interpreted by the average ionic radii of alkaline metals: \( r(\text{average}) = X(\text{Li}_2\text{SO}_4) r(\text{Li}) + X(\text{R}_2\text{SO}_4) r(\text{R}) \), where \( r \) and \( X \) denote, respectively, mole fraction and the ionic radii of alkaline metal. The oxygen anion activities would increase with an increase in \( \text{R}_2\text{SO}_4 \) mole fractions of binary sulfates \( \text{Li}_2\text{SO}_4 + \text{R}_2\text{SO}_4 \).

I. INTRODUCTION

The disposal of garbage is normally based upon combustion in refuse burners. In such incineration systems, alloys are inevitably brought into contact with oxidizing atmosphere. In oxidizing gases, metals and alloys can be protected from oxidation by the formation of an adherent, slow growing oxide film, generally comprised of Cr₂O₃, Al₂O₃, and SiO₂. The combustion product gas in refuse incinerators, however, contains inorganic impurities such as sulfur and chlorine. Because of such impurities, when the gases are cooled, fused salt film may condense on the hardware to generate a highly corrosive condition, corresponding to accelerated degradation known as "hot corrosion."

As pointed out by Rapp, an important initial aspect of hot corrosion is the consideration of thermodynamic stability of protective oxides and fused salts. Under the presence of fused salt, such oxide exhibits limited stability. Figure 1, cited from the review paper of Rapp, indicates the phase stability of the Na + Cr + S + O system at 1200 K. Fused Na₂SO₄ is frequently a major constituent of corrosive fused salt because of its high thermodynamic stability coupled with the general presence of Na and S in refuse burners.

Within the Na₂SO₄ stability field, Cr₂O₃ may react and dissolve into Na₂SO₄ to form corrosion products, depending upon the partial pressure of O₂ and the activity of O²⁻. The dissolution of Cr₂O₃ (s) into Na₂SO₄ (l) can be expressed as

\[
\text{Cr}_2\text{O}_3 (s) + (3/2)\text{O}_2 (g) + 2\text{O}^{2-} = 2\text{CrO}_4^{2-} \quad [1]
\]

where \( a(i) \) denotes the activity of \( i \). It follows, from Eqs. [3] and [4], respectively, that at a fixed oxygen partial pressure,

\[
d \log \{a(\text{CrO}_4^{2-})\}/d \log \{a(\text{O}^{2-})\} = +1 \quad [5]
\]

\[
d \log \{a(\text{Cr}^{3+})\}/d \log \{a(\text{O}^{2-})\} = -3/2 \quad [6]
\]

Attention, hence, can be focused on measurable quantities of \( a(\text{Na}_2\text{O}) \) rather than \( a(\text{O}^{2-}) \). For the experimental determinations of the \( \text{Na}_2\text{O} \) activities, pure \( \text{Na}_2\text{SO}_4 \) would be brought into equilibrium with gas mixtures of \( \text{SO}_2 + \text{O}_2 \);

\[
\text{Na}_2\text{O} (\text{salt}) + \text{SO}_2 (g) + (1/2)\text{O}_2 (g) = \text{Na}_2\text{SO}_4 (\text{salt}) \quad [8]
\]

\[
\text{Cr}_2\text{O}_3 \quad \text{Na}_2\text{SO}_4 \\
\text{Cr}_2\text{O}_3 \quad \text{Na}_2\text{SO}_4 \\
\]
In an alternative approach, sodium-beta-alumina and stabilized zirconia can be employed to measure chemical potentials of Na and O2, respectively, within pure Na2SO4. They also determined the solubilities of Cr2O3 in pure Na2SO4, as shown in Figure 2. It is noted that the abscissa in Figure 2 is log(a(Na2O)) rather than log(a(O2-)). The relations between log(solubility of Cr) and log(a(Na2O)), nevertheless, are essentially linear with the slopes of +1 and -3/2, respectively, in conforming to Eqs. [5] and [6].

Next, consider binary sulfate melts of Li2SO4 + Na2SO4. Lithium sulfate is also a major component of fused salt in hot corrosion. The activities of oxygen anion depend upon mole ratios of Li2SO4/Na2SO4. For the binary sulfates, neither $a$(Li2O) nor $a$(Na2O) can be related to $a$(O2-), although the activities of Li2O and Na2O in binary Li2SO4 + Na2SO4 melts are, in principle, measurable.

For a relative or semiquantitative measure of oxygen anion activities, an alternative approach is the use of RedOx equilibria such as Cu2+/Cu+, Fe3+/Fe2+, Cr3+/Cr4+, and Mn4+/Mn2+ couples. An excellent overview on RedOx equilibrium in silicate melts can be found in a book by Turkdogan.86 For molten silicates, experimental determinations of RedOx equilibrium can be made by equilibrating oxide melts with a stream of fixed oxygen partial pressures. For sulfate melts, RedOx measurements require gas mixtures of fixed O2 and SO2 potentials. The activities of oxygen anion in sulfate melts are connected to the chemical potentials of SO2 and O2 via reaction:

$$\text{SO}_2 (g) + \frac{1}{2} \text{O}_2 (g) + \text{O}^{2-} (\text{melt}) = \text{SO}_4^{2-} (\text{melt}) \quad [10]$$

In the present study, gas mixtures of Ar + O2 + SO2 with $P_{O_2}$ = 10^3 to 10 Pa (10^-2 to 10^-4 atm) and $P_{SO_2}$ = 10 Pa (10^-4 atm) were used for the equilibrium experiments. These commercially available gas mixtures contain relatively small concentrations of SO2, hence minimizing potential hazards in the laboratory.

For these gas mixtures, a few words seem to be pertinent with respect to the choice of RedOx couple. Figure 3 shows the potential diagram of the systems alkali metal + oxygen + sulfur at 973 K. In this diagram, line A corresponds to the equilibrium reaction [11] at $P_{SO_2}$ of 10 Pa (10^-4 atm),

$$(1/2)\text{S}_2 (g) + \text{O}_2 (g) = \text{SO}_2 (g) \quad [11]$$

while solid circles represent the gas mixtures of Ar + O2 + SO2 used in this study. In Figure 3, the equilibrium oxygen partial pressures of mixtures CuO + Cu2O, FeO + Fe2O3, and SnO + SnO2, with unit activities, are also expressed by horizontal arrows. As can be seen from Figure 3, at the partial pressures of O2 and SO2 used in this study, the ratio Cu2+/Cu+ would be detectable via chemical analysis, whereas with Fe3+/Fe2+ and Sn4+/Sn2+ couples, concentrations of Fe2+ and Sn2+ would be too small to be determined with satisfactory accuracy.

The equilibrium reaction underlying the present study can be expressed by

$$\text{Cu}^+ + \frac{1}{4} \text{O}_2 (g) = \text{Cu}^{2+} + \frac{1}{2} \text{O}_2^{-} \quad [12]$$

or

$$\text{Cu}^+ + \frac{1}{4} \text{O}_2 (g) + \frac{3}{2} \text{O}^{2-} = \text{CuO}_2^{-} \quad [14]$$

At any given temperature, the activities of Na2O can be determined by knowing $P_{O_2}$ and $P_{SO_2}$.

In an alternative approach, sodium-beta-alumina and stabilized zirconia can be employed to measure chemical potentials of Na and O2, respectively, within pure Na2SO4 melts. Experimental determinations of the Na2O activities based upon such electrochemical measurements were first conducted by Rapp and co-workers3,8 and Zhang67 for...