RECOVERY OF ALUMINUM FROM SECONDARY SOURCES
BY MEANS OF AGITATED MOLTEN SALT

B. J. Racunas
Aluminum Company of America
Alcoa Laboratories
New Kensington, Pennsylvania 15068

Abstract

Aluminum recovery from secondary sources in agitated molten salt is a three-step process: (1) separation of aluminum from the non-metallics, (2) coalescence of the separated aluminum, and (3) removal of the non-metallics from the system. Separation of aluminum from non-metallics is enhanced by promoting interfacial tension conditions that maximize the negative surface free energy change. Metal coalescence is promoted by minimizing the product of the rate of shear and the viscosity of the non-metallics, salt slurry in the agitated molten salt environment. Centrifugation is analyzed as a means of removing insoluble particulate from the molten salt.

It has long been recognized that mixtures of certain chloride and fluoride salts provide a fluxing action that can promote the recovery of aluminum metal from secondary aluminum sources. These secondary aluminum sources can range from high metal content scrap, such as scalpings, trimmings, powder and sawdust, to sources more highly contaminated with non-metals, such as furnace skim or dross. In separating and recovering aluminum from secondary materials, several methods employing salt have commonly been used. One method applied to skim or dross treatment involves the use of a rotary barrel in which the skim or dross is deposited and tumbled together with a small amount of dry salt flux. Another method makes use of a rotary salt furnace in which a substantial amount of liquid molten salt and the scrap metal materials are rotated about a horizontal axis.

Both these processes are essentially batch operations, consisting of (1) charging the rotary device with the secondary aluminum source and salt, (2) rotating for a given time period, (3) tapping the recoverable aluminum, and (4) discharging the residue consisting of spent salt, unrecov-
ered aluminum metal, and aluminum oxide and other solid non-metallics.

Another molten salt method for aluminum recovery consists of circulating molten salt by means of a pump to melt aluminum scrap. This process requires periodic shutdowns to remove accumulated non-metallics, thus limiting its application to high metal content secondary aluminum sources.

It would be advantageous to have a molten salt process designed to effect continuous or nearly continuous removal of solid particulate separated from the aluminum source.

This paper describes theoretical considerations for a potential method for achieving this goal, using agitators to keep non-metallic solids in suspension and an immersed centrifugal device to remove particulate.

Aluminum recovery from secondary sources in an agitated molten salt environment is basically a three-step mechanism: (1) separation of aluminum from its oxide and other non-metallics, (2) coalescence of the separated aluminum into droplets or globules large enough to settle out of the salt bath and into a metal pad at the bottom of the vessel, and (3) separation and removal of the non-metallic particulate from the molten salt bath.

For the first step, the stripping of the non-metallic skin from the metal, the surface free energy for removal of the adhering films must be favorable. The change in surface free energy for detachment of the oxide and other non-metallics from aluminum in a molten salt bath is given by:

\[ \Delta F = \sigma_{BM} + \sigma_{BO} - \sigma_{MO} \]

For \( \Delta F \) negative, it follows:

\[ \sigma_{MO} > \sigma_{BM} + \sigma_{BO} \]

Optimum separation occurs when \( \sigma_{MO} \) is maximized and \( \sigma_{BO} \) and \( \sigma_{BM} \) are minimized. It is evident that when these conditions occur, \( \Delta F \) is at its highest possible negative value.

Zhemchuzhina and Belyaev(2) investigated surface tension effects with regard to stripping the oxide film from aluminum in chloride-based molten salts containing varied
fluoride concentrations. According to their findings:

1. Suspended particles of Al₂O₃ in a molten salt bath increase \( \sigma_{BM} \) and \( \sigma_{BO} \).
2. Dissolving Al₂O₃ as a surface active component lowers \( \sigma_{BM}, \sigma_{BO} \).
3. \( \sigma_{MO} \) increases with small additions of fluorides
4. \( \sigma_{BO} \) increases with large fluoride additions.

Applying these effects to equation (2), it is apparent that separation of metal from oxide is: (a) enhanced by a small fluoride addition to the bath, (b) made more difficult by oxide suspended in bath, (c) made more difficult by an excessive fluoride concentration, and (d) more easily accomplished as the ratio of metal/non-metallics in feed increases.

Sully, Hardy and Heal\(^{(3)}\) investigated thickening and metal entrapment in light alloy melting flux. They found that oxide particles in a bath thickened or increased the viscosity of 90:10 NaCl-CaF₂ considerably more than would be expected from equations relating slurry viscosity to the volume concentrations of spherical particles. It was suggested that the form of the oxide in the molten salt was important. The flat, plate-like shape of the non-metallic particles in their system caused a high degree of thickening. On the other hand, ball-milled and spherical forms of alumina caused significantly less thickening when added to the flux. The shapes of these more spherical particles more closely approached the shapes of the particles on which the classical slurry equations were based. The investigators also found that stirring led to the apparent thinning of the flux and assisted agglomeration of metal particles trapped in the thickened flux, suggesting the fluid has thixotropic tendencies. Viscosity of a molten salt-oxide or other non-metallics slurry therefore is a function of particle shape, particle concentration, shear forces and position relative to the agitating device.

Karam and Billinger\(^{(4)}\) discuss factors affecting the drop size of the discontinuous phase in a simple shear field where two immiscible liquids are present. They review Taylor's\(^{(5)}\) work in this area, which holds that the disruptive forces due to viscosity tending to burst a droplet of the discontinuous phase are about equal to the forces due to interfacial tension tending to hold it
The drop size of the discontinuous phase was then related to system properties by the following equation.

\[
(3) \quad d = \frac{32 \sigma}{G \mu_c} \left( \frac{\mu_c + \mu_d}{16\mu_c + 19\mu_d} \right)
\]

This relationship can be applied to the molten aluminum, molten salt, and insoluble non-metallics system by substituting molten aluminum metal for the discontinuous phase and the molten salt-non-metallic particulate slurry for the continuous phase. Since the oxide-laden molten salt viscosity is significantly greater than the metal viscosity, the stable metal droplet size can be approximated by the following relationship:

\[
(4) \quad d_m = \frac{K'\sigma_{BM}}{G\mu_b}
\]

To maximize the stable metal droplet diameter at a given insoluble non-metallic solids concentration in the molten salt bath, the product \(G\mu_b\) in the above equation must be kept at a minimum. Since the bath-insoluble non-metals slurry is thixotropic, \(\mu_b\) is an inversely proportional function of \(G\), and an optimum stirrer or agitator speed that minimizes the product \(G\mu_b\) exists.

This droplet size relationship is most significant when the metal droplets being generated are small and the non-metallic particulate concentration is substantial. Under these conditions, the metal droplets may settle through the salt pool at about the same rate as the insoluble non-metallic particles once the agitation effect is decreased or interrupted. This condition prevents the formation of a coalesced metal pad at the bottom of the separation vessel.

Obviously, non-metallic particulate concentration is of prime importance. It has been demonstrated that an increased solids loading affects interfacial relationships and causes exponential increases in bath viscosity. These surface tension and viscosity conditions, in turn, determine the size of metal droplet formed and the extent of metal recovery.

Figure 1 indicates the effect of fluoride content and relative agitator speed on aluminum recovery from cold dry furnace skim. The graph indicates that maximum recovery was attained when approximately 5% cryolite was added to the basic NaCl-KCl molten salt bath. At a 3:1 ratio of molten salt to dry skim charge, higher rotational speed resulted in recovery of nearly all of the metal available.
in the charge. Further tests showed that, at still higher rotational speeds with a high concentration of non-metallics in the salt, a situation could be achieved in which a stable metal in salt emulsion was formed. Metal spheres formed in this fashion were so small as to be visible only under a microscope. The droplets of aluminum in the salt were sufficiently small and the concentration of oxides in the salt was high enough that coalescence was impaired.

A small initial aluminum feed particle size, however, does not necessarily rule out droplet coalescence and growth. Table 1 indicates the extent of metal recovery in agitated molten salt baths for a number of secondary aluminum feed materials. The table shows, in general, that a high degree of aluminum recovery is attainable in agitated molten salt for a wide range of secondary aluminum source materials. The phenomenon of aluminum droplet coalescence and growth is best indicated by the high degree of aluminum recovery from extremely fine aluminum powder. Table 1 indicates that over 84% gross aluminum recovery in a coalesced metal pad was achieved from -325 mesh aluminum powder feed.

Table 1
Metal Recovery in Agitated KCl-NaCl Cryolite Baths

| Feed                  | % Metal in Feed By Analysis | Gross % Al Recovered | % Available Al Recovered |
|-----------------------|-----------------------------|----------------------|-------------------------|
| Rotary Barrel Residue | 48                          | 41                   | 85                      |
| Cold, Dry Skim        | 55                          | 55                   | 99+                     |
| Hot, Wet Skim         | --                          | 87                   | 90+                     |
| Coarse Al Powder (+40 mesh) | --                      | 97.7                 | 98+                     |
| Fine Al Powder        | --                          | 84.5                 | --                      |
| 90% (-325 mesh)       | --                          | --                   | --                      |

Thus far we have examined the phenomena related to the separation of aluminum from its oxides and other non-metallics in an agitated molten salt environment. We have also proposed a relationship governing the formation and stabilization of discrete aluminum droplets in the molten
salt bath. What remains is to consider the removal of the oxide and other non-metallics from the salt. Non-metallic particulate in the molten salt conceivably could be removed by settling and decanting, filtration or centrifugation. One technique, shown to be applicable in the removal of insoluble particulate from molten salt, is the use of a centrifugal device immersed in the molten salt and containing integral pumping means for causing a net flow of slurry through the device. When the centrifuge bowl is rotating, particulate matter enters through the holes in the bottom of the structure and is diverted by centrifugal force to the sidewalls where it collects as a concentrated sludge.

Consider an oxide particle P with diameter $D_p$ entering a simplified version of such a centrifugal device at a distance $r$ from the central axis of rotation $a$.

Assume the particle will be collected if it is diverted by centrifugal force to position $r_c$ before it traverses $L$, the length of the centrifuge. Assuming further that Stokes Law holds, the settling velocity for the particle in the radial direction is given by:

\[
\frac{dr}{dt} = \frac{(\rho_p - \rho_b)D_p^2 \omega^2 r}{18 \mu_b}
\]

The velocity in the axial direction is given by:

\[
\frac{d\bar{a}}{dt} = \frac{QL}{\pi r_c^2 L} = \frac{Q}{\pi r_c^2} = \frac{Q}{A}
\]
Dividing equation (5) by equation (6)

\[ \frac{dr}{d\theta} = \frac{(\rho_P - \rho_b)D_p^2 \omega^2 rA}{18 \mu_b Q} \]

and integrating,

\[ \int_0^L d\theta = \int_r^{r_c} \frac{18 \mu_b Q \ dr}{(\rho_P - \rho_b)D_p^2 \omega^2 rA} \]

gives

\[ L = \frac{18 \mu_b Q}{(\rho_P - \rho_b)D_p^2 \omega^2 A} \ln\left(\frac{r_c}{r}\right) \]

Rewriting equation (9)

\[ r = r_c / \exp\left[ \frac{(\rho_P - \rho_b)D_p^2 \omega^2 AL}{18 \mu_b Q} \right] \]

where \( r \) is the smallest inlet radius at which a particle of diameter \( D_p \) will be diverted to position \( r_c \) by centrifugal force and be collected to the bowl.

This relationship indicates that the likelihood of particle capture is enhanced by increases in particle size, density difference between the particle and the molten salt, centrifuge rotational speed and the distance of particle entry point from the centrifuge central axis.

The above simplified mathematical model is by no means a rigorous treatment of the forces acting on a particle passing through a centrifugal device immersed in molten salt. It does, however, offer insight into the qualitative workings of the device and gives some criteria for submerged centrifuge design and operation.

In summary:

1. Previous work relative to the use of molten salt in the recovery of aluminum from secondary sources has been reviewed, and a mechanism for the separation of aluminum from non-metals in an agitated molten salt environment has been suggested. Conditions tending to maximize the
negative free energy for separation enhance the probability of metal recovery.

2. Metal droplet size in an agitated molten salt shear field depends to a great degree on the molten salt-non-metallic particulate slurry viscosity and stirring characteristics. An increase in the non-metallic particulate concentration affects interfacial relationships and causes exponential increases in bath viscosity. Thus, solids loading is a prime factor determining the extent of aluminum recovery in a molten salt environment.

3. A method for removing solid non-metallic particulate from molten salt by means of a submerged centrifugal device has been described. An analysis of the qualitative workings of the device was considered to identify system properties, design features, and operating characteristics affecting performance.

References
1. Adamson, A., "Physical Chemistry of Surfaces," Inter-science Pub., N.Y., 1970, p 372.
2. Zhemchuzhina, E.A., and Belyaev, A.I., "Surface Phenomenon and the Adsorption of Aluminum Oxide by Fluxes," Chem.Abs. 54, 19379a.
3. Sully, A. H., Hardy, H.K., and Heal, T.J., "An Investigation of Thickening and Metal Entrapment in a Light Alloy Melting Flux," J. Inst. Metals 82, 1495 (1953-54).
4. Karam, H.J. and Bellinger, J.C., "Deformation and Breakup of Liquid Droplets in a Simple Shear Field," I & EC Fundamentals, 7, No. 4, Nov. 1968.
5. Taylor, G.T., Proceedings Royal Soc. (London) Series 138A 41 (1932).

Nomenclature

ΔF = surface free energy
σ_{BM} = interfacial tension between salt bath and metal
σ_{BO} = interfacial tension between salt bath and non-metallic skin
σ_{MO} = interfacial tension between metal and non-metallic skin
d = effective discontinuous phase droplet diameter
\( d_m \) = effective diameter of stable metal droplet
\( K \) = constant
\( G \) = shear rate
\( \mu_d \) = viscosity of discontinuous phase
\( \mu_c \) = viscosity of continuous phase
\( \mu_m \) = viscosity of metal droplet
\( \mu_b \) = viscosity of salt bath-nonmetallics slurry
\( r \) = distance from centrifuge axis of rotation
\( r_c \) = position to which a particle must be diverted for collection
\( \rho_p \) = density of solid particulate
\( \rho_b \) = density of molten salt bath
\( D_p \) = particle diameter
\( \omega \) = angular velocity
\( Q \) = volumetric flow rate
\( L \) = centrifuge length in direction of flow
\( A \) = effective centrifuge flow cross sectional area
FIGURE 1

AI RECOVERY FROM 55% METAL CONTENT DRY SKIM

1 170 RPM, 3:1 KCl-NaCl BATH TO SKIM WT. RATIO
2 90 RPM, 3:1
3 90 RPM, 1:1
4 170 RPM, 1:1

% AVAILABLE AI RECOVERED IN COALESCED PAD

% CRYOLITE ADDED TO KCl-NaCl BATH

% GROSS AI RECOVERED IN COALESCED PAD