

Impact of Cooling Water Composition on Heat Transfer in Ingot Casting

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Abstract

It has long been known that variation in the composition of ingot cooling water can have an effect on the casting process. These effects can include discoloration, cracking, excessive curl and bleedouts. While several studies have been conducted to understand heat flux in ingot casting, there information in the literature is limited relating specific chemical species or interactions to heat transfer or relating specific solution properties to boiling heat transfer. In an effort to gain insight into the relationships between water chemistry and heat transfer, a broad literature review was conducted. Upon examining the literature beyond aluminum ingot casting, many examples were found in which components of cooling water had very different effects dependent on the heat transfer regime. This paper serves to summarize many of the findings in the literature and to propose mechanisms for the effects of cooling water composition seen in aluminum DC casting. A good deal of information was discovered in reviewing literature published related to the power-generation industry.

Introduction

Recent research involved a series of statistically designed experiments in an effort to quantify the effects of some commonly measured water chemistry parameters on heat transfer in aluminum DC casting. The apparatus used in the experiments has been described elsewhere [1]. Initial results of these tests were not fully consistent with results previously published in the literature [2], [3], [4]. Notably, qualitative relationships between heat flux and alkalinity, hardness, or other parameters were not reproducible and showed significant variability. As stated by Grandfield [3], the complexity of heat transfer mechanisms and interdependence with solution properties (water chemistry) make straight-forward relationships difficult, at best, to establish.

There are a number of commonly measured parameters that are monitored and reported in Alcoa's Ingot Plant recirculating water systems. Many of these parameters have been chosen because of the existence of quick, inexpensive techniques to measure them. However, some of these parameters are easily confused, redundant, and may not be effective indicators of how the cooling water will affect aluminum ingot casting. A brief review of these parameters is in order.

Commonly Measured Parameters in Ingot Cooling Water

Hardness

Hardness is the result of multivalent cations (principally Mg^{2+} and Ca^{2+}) in aqueous solution. These ions occur in cooling water as a result of primarily natural but also some man-made conditions. Rainwater and groundwater containing dissolved CO_2 will

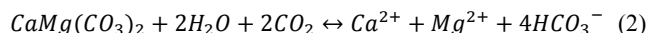
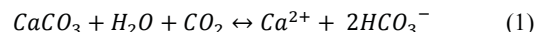
dissolve magnesium and calcium from minerals such as calcite ($CaCO_3$), gypsum ($CaSO_4 \cdot 2H_2O$), and dolomite ($CaMg(CO_3)_2$). Because of variation in geologic structure and composition, hardness of surface- and ground-water can exhibit a wide range of values. Hardness is typically reported in units of ppm $CaCO_3$, although total hardness is often broken into both Mg and Ca components.

The source of cooling water for ingot casting operations largely determines the range of hardness in Alcoa's recirculating water systems. Hardness is increased in a recirculating system through evaporative losses and then decreased through blowdown and makeup water addition. The ratio of blowdown concentration to makeup water concentration is known as "cycles of concentration".

Several sources [2], [3] have reported that overall quench rate increases with hardness by affecting boiling phenomena at and at high levels. Another source reported quench rate decreases with hardness in the convective regime [5]. Hardness is relatively easy to control through blowdown but is limited by the makeup water hardness. Hardness can be more actively controlled through softening or reverse osmosis treatment.

Alkalinity

Alkalinity is a measure of the buffering ability of an aqueous solution. It is the result of dissolved bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions and CO_2 . Like hardness, the natural sources of alkalinity are the dissolution of calcite and dolomite by the following reactions, respectively:



As a result, alkalinity levels in water often trend with hardness. Alkalinity is typically reported in units of ppm $CaCO_3$ equivalent. Significant variation in alkalinity of surface and subsurface waters exists throughout the United States [6].

Yu [2] reported that quench rate is inversely proportional to alkalinity, i.e. lower alkalinity increases heat transfer and that at high levels it can affect boiling. Alkalinity is relatively easy to control through additions of sulfuric acid (H_2SO_4).

Conductivity, Total Dissolved Solids and Ionic Strength

Boiling is a two-phase phenomenon. Because the water molecule is polar, its boiling behavior can be strongly affected by dissolved ionic species or surface active agents [2].

Conductivity, Total Dissolved Solids (TDS) and Ionic Strength are measures of the dissolved ions and molecules in water which affect its ability to conduct electrical current. Yu [2] and

Grandfield [3] stated that water quench rate increases with conductivity. Increasing ionic strength or conductivity has been reported to generally inhibit bubble coalescence during boiling [7] which increases heat transfer by promoting nucleate boiling [2]. This is likely to be due to stabilizing the electrical double layer around the water vapor bubble, thereby inhibiting bubble coalescence [8]. However, anionic polyelectrolytes and alkaline species reduce boiling heat flux by promoting bubble coalescence [2].

Helali [9] has reported reduction in flow boiling heat transfer due to increased solution viscosity from dissolved salts. Najibi and Muller-Steinhagen [10] have agreed that some dissolved solids (notably CaSO_4) reduce the heat transfer in flow boiling by further increasing ionic strength while dissolution of other species such as NaCl increases heat transfer.

Conductivity or ionic strength has only small effect on the boiling temperature itself [7] [11]. Because of this fact, elevation or depression of the boiling point is not a likely mechanism for changes in boiling heat transfer in ingot casting.

Surfactants

Surfactants significantly reduce surface and interfacial tension of water and water/solid interfaces. This leads to greater wetting of the solid surface and inhibits bubble coalescence during nucleate boiling, increasing heat transfer dramatically [7] [12]. However in the film boiling regime surfactants stabilize the film [2], thus inhibiting collapse of the steam film and reducing heat transfer.

The combination of the two effects cited above may serve to make the transition from film to nucleate boiling more severe and abrupt.

Total Suspended Solids

Total suspended solid (TSS) is a measure of non-soluble particles in the water. This is usually addressed through filtration and/or settling. Silt, rust, and scale are primary contributors to TSS. In general, water quenchability is inversely proportional to TSS.

Suspended solids provide nucleation sites and reduce the superheat required for boiling to occur. The effect is to stabilize film boiling down to lower temperatures, inhibiting heat transfer [2] in casting processes not utilizing the A729 (CO_2 injection) process. For operations that do rely on the A729 process, the opposite holds true as the solids promote heterogeneous precipitation of the CO_2 bubbles.

Oil and Grease

Oil and grease suspended in the casting cooling water can come from hydraulic leaks, mold lubricant, and mold and bottom block grease. Its effect has been found to be similar to TSS.

Turbidity

Turbidity arises from both TSS and oil and grease. It is a measure of light-scattering effects of the total non-soluble particles in the cooling water. Its effect is the same (perhaps a sum) as the effects of its components and so quenchability varies inversely with turbidity.

pH

It is unclear what direct effect pH has on cooling water quenchability, but many anecdotes exist which suggest that it does have an effect. It may be that pH itself does not influence heat transfer, but it is well-known that changes in pH can affect the solubility of dissolved chemicals. If solubility is shifted enough to effect precipitation of a solid or evolution of a gas, these events may indeed affect local heat transfer significantly.

Dissolved Gases

Several common atmospheric gases are soluble in liquid water. These include CO_2 , O_2 , and N_2 . Under normal operating conditions, ingot cooling water is likely to be saturated with air when passing through the cooling tower [2]. Several other highly soluble gases are products of biological processes, but are not normally present at significant concentrations in the makeup water sources of Alcoa's ingot plants.

Dissolved gases lower the boiling temperature of water and promote stable film boiling [7]. They reduce the wall superheat at boiling and the Leidenfrost temperature. Boiling occurs when the total pressure ($P_{\text{H}_2\text{O}} + \sum P_{\text{dissolved gases}}$) exceeds atmospheric pressure. Since gas solubilities are inversely dependent on temperature, dissolved gases evolve from the water during the heating and boiling that occurs during cooling water contact with the hot ingot surface. The solubility of CO_2 at 80 F is approximately 1.4 g/l and is the highest of the atmospheric gases. CO_2 is also produced when water with significant alkalinity levels is heated through the decomposition of bicarbonate [7] [13]. Additionally, in several of Alcoa's ingot plants, CO_2 is injected into the cooling water using the A729 process specifically to control butt curl by promoting film boiling at the start of casting [14].

Findings and Discussion

Effects of aqueous species on properties and boiling

The most commonly discussed compositional parameters include alkalinity, hardness, conductivity, total suspended solids, turbidity, and total dissolved solids. These parameters are the most commonly measured in Alcoa's ingot cooling water treatment systems. A number of plant-specific "rules of thumb" exist regarding their effect on ingot cooling. However, as increasingly difficult-to-cast alloys are developed and as casting practices become more complex, it has been found that these rules are not universal.

While numerous studies have been conducted to understand heat flux in ingot casting, there is scant information in this literature relating specific chemical species or interactions to heat transfer or relating specific solution properties to boiling heat transfer. For this reason it has been necessary to broaden the literature review beyond the ingot casting process.

The literature included many examples in which components of cooling water had quite different effects dependent on the heat transfer regime (film boiling, nucleate boiling, forced convection and free falling convection) under investigation.

Dissolved gas reduces the wall superheat in nucleate boiling, enhancing heat transfer at low heat flux [7] [13]. However, it can significantly reduce the Leidenfrost temperature and stabilize film boiling. The effect on film boiling is precisely the reason for the A729 process [14].

During convective heat transfer, dissolved solids have general effect of reducing heat transfer as ionic strength increases [5] [15] [11]. In transition and nucleate boiling, electrolyte solutions generally have lower heat transfer coefficients than pure water, except at very high heat fluxes in which the reverse was true [10] [11]. Increasing levels of dissolved inorganic salts increase Leidenfrost temperature and reduce stability of a steam film.

Suspended solids have the effect of reducing superheat during nucleate boiling. Suspended particles serve as nucleation sites for vapor bubbles. This serves to promote film boiling in water without additions of CO₂. In cooling systems utilizing CO₂ for butt curl control, the particles have the opposite effect and in effect “short circuit” the effect so that the gas evolves before contacting the ingot. Surfactants were found to increase boiling heat transfer in the nucleate boiling regime, but also stabilize the film during film boiling [2] [7] thus tremendously reducing heat transfer.

In ingot casting the convective heat transfer is of much less importance than boiling heat transfer. During the initial stages of ingot casting, it is often of primary importance to establish film boiling and then “wash off” the steam film under controlled conditions. Following the extinguishing of the steam film, nucleate boiling becomes the primary heat transfer mechanism through steady state. For those alloys and ingot sizes that do not rely on film boiling, the ability to control nucleate boiling heat transfer is very important.

Physical properties affecting boiling heat transfer

Boiling is a two phase-phenomenon in which a liquid changes to a gas, creating a surface between the two. In ingot casting this occurs at another surface, that of the solid ingot surface which is at very high temperature relative to the cooling water. Because boiling occurs when the total vapor pressure of the liquid exceeds the localized atmospheric pressure [2], it is affected by several properties of the liquid and conditions at the interface. Furthermore, the same properties - and additionally those of the gas and solid - affect how heat is transferred from solid to the cooling water during boiling. The physical properties most often mentioned in the literature include surface/interface tension and viscosity.

In ingot cooling there are three important surfaces or interfaces. These are the solid/liquid (SL), liquid/vapor (LV), and the solid/vapor SV interfaces. Each interface has an associated energy that scales with its area. The nature of each interface plays a role in boiling heat transfer.

Surface tension (or surface energy, γ_{LV}) is the energy stored or needed to create a free surface in a condensed phase. Condensed phases are typically at lower free energy when they are in a bonded (primary or secondary) state. To create a surface, a certain number of bonds must be broken which costs energy.

In boiling, new surfaces are continuously being created and the energy penalty is “paid for” by the absorption of heat, in the case of casting, from the ingot. A system comprised predominantly of fine dispersed bubbles in boiling water has much higher surface area than one which is dominated by large bubbles or by continuous film of vapor. To minimize surface energy of the boiling water, it is expected that a solution with higher surface tension would tend to minimize bubble surface area. This occurs by the bubbles remaining as relatively rigid spheres rather than distorting. Because they undergo little distortion, coalescence of high surface tension bubbles is governed by the proximity of the nucleation sites and size of the bubbles prior to detachment [15].

When detached from a superheated wall small bubbles are more likely than large bubbles to recondense in the bulk liquid [16]. Upon recondensing, the small bubbles release the heat of vaporization and surface energy back to the bulk, heating the water. In contrast, large bubbles escaping to the free surface release much of their stored energy to the atmosphere as steam and transfer less heat to the water. This is an example of why the mode of boiling (film, transition, or nucleate) is important in ingot casting, and especially the transition from one mode to another.

Interface Tension, Wetting, Contact Angle

While surface tension is often measured or stated in terms of a gas/liquid interface, the term “interface tension” is often used when considering boundaries between condensed phases whether liquid/liquid or liquid solid. Interface tension is a measure of the attraction of two dissimilar substances such as aluminum and water. In boiling, interface tension determines whether bubbles are more likely to stay in place on the surface, or to detach. When bubbles stay in place on the surface and coalesce to form larger bubbles or a film, they inhibit heat transfer. Detachment of the bubble allows the water to again contact the surface and quench the metal. Interface tension and wetting are intimately related. The wetting contact angle is often used as a measure of interface tension. Contact angle is well-known to be temperature dependent.

Wetting behavior and interface tension were often discussed in the literature as being influential on boiling heat transfer [2] [17] [18] [11] [19] [16] [20] [21]. These properties affect nucleation, growth rate, departure size and departure frequency in boiling heat transfer and thus greatly influence both critical and transition heat fluxes.

Bernardin, *et al* [19] found that small degrees of organic or inorganic contamination on aluminum surfaces caused wide variation in contact angle and by extension, boiling heat transfer. Jamialahmadi and Muller-Steinhagen [15] focused on the effects of calcium sulfate (CaSO₄) deposition. They reported that interface tension between depositions of calcium sulfate and the solution were much lower than that between the solution and bare metal surface. Because of this, deposits formed on the metal surface become active nucleation sites which create small spherical bubbles and increases heat transfer. Other deposits such as CaCO₃ and Mg(OH)₂ were also mentioned. Formation of these deposits is possible even in relatively dilute solutions because of the localized increase in concentration of solute during the boiling event. It has been estimated that concentrations at the vapor/liquid interface can increase by a factor up to 10⁴ [21] thus

exceeding the solubility. The resulting deposits locally alter the wettability of the surface.

Surface Tension

Many of the papers reviewed cited surface tension as being influential on the boiling characteristics [2] [7] [15] [10] [11] [12] [22] [16] [21]

Surface tension of water generally increases with additions of salts. Thermodynamically, increasing surface tension favors formation of fewer, larger vapor bubbles and higher superheat to nucleate the bubbles. This is confirmed in the works of Cui [7] [13] and Jamialahmadi, [15] [11] [21]. Cui stated that in nucleate boiling, dissolved Na_2CO_3 reduced nucleation density and prevented coalescence of bubbles thus increasing heat transfer. Jamialahmadi found the same to be true with aqueous solutions of Na_2SO_4 . Marrucci and Nicodemo [8] concluded that inorganic electrolytes with a higher dy/dc (surface energy versus concentration slope) have a stronger inhibition of bubble coalescence. However, even at high concentrations of inorganic electrolytes, surface tension, viscosity and density change by only a few percent.

Najibi, *et al* [10] and Yu [2] stated that dissolved salts lower interface stability in aqueous solutions and Harada [16] found that surface tension plays an important role in bubble detachment and transfer of thermal energy to the liquid through subsequent collapse of the bubble.

Surfactants were shown to reduce heat flux by promoting film boiling. This occurs through their ability to increase the stability of the interface [2]. Inversely, surfactants increase heat transfer in nucleate boiling [7] by improving wettability between liquid and solid. Anionic surfactants may include some sulfates and phosphates.

CO_2 is noted by Sagert and Quinn [23] to be surface active and to considerably depress the surface tension of water. Bubble coalescence times were reported to be very short (<3 ms) at relatively low pressures near atmospheric. However, Cui [13] claimed that dissolved CO_2 has no effect on surface tension but did have a large effect on bubble nucleation, growth and coalescence.

Viscosity

Coolant viscosity may have a small inverse relationship with boiling heat transfer [12], in that it affects detachment of the bubbles from the surface and the contact and spread of the water. However, in the case of ingot casting the extremely small variation in viscosity is unlikely to play a significant role.

Surface Potential and Bubble Coalescence

Bubble coalescence is not a property in itself but rather a phenomenon that has a large influence on boiling heat transfer and steam film formation. Increasing tendency of bubble coalescence promotes film boiling, [2] while resistance to coalescence favors nucleate boiling.

Bubble coalescence depends upon surface tension, on both the concentration and valence of the dissolved electrolyte present in

the cooling water, and the magnitude of the dy/dc (surface energy versus concentration) derivative [8]. It was widely reported in the literature that dissolved inorganic salts inhibited coalescence of vapor bubbles [2] [7] [10]. Inorganic electrolytes of higher valence inhibit coalescence more than monovalent ions. Marrucci, *et al* and others concluded that this effect was due to electrical repulsive forces from the dissolved ions [8] [24]. Yu found that soluble cations tend to inhibit bubble coalescence promoting nucleate boiling. Anions have the opposite effect and retard boiling heat transfer [2].

The stability of the steam interface in film boiling is also affected by the solution viscosity and density. However, as stated earlier, in ingot cooling water the variation of viscosity and density are unlikely to be large enough to play a significant role in heat transfer variation.

Nucleation and growth of vapor bubbles

At its simplest, boiling is a phase transformation involving nucleation and growth phenomena. To boil water, the activation energy must be overcome to nucleate vapor bubbles. The activation energy can be raised or lowered by conditions at the heat transfer interface such as roughness, wettability or superheat, by dissolved or heterogeneously mixed chemical species in the water, and by surrounding conditions such as atmospheric pressure. These factors have quite different effects on heat transfer, depending on the regime (film-, transition-, nucleate-boiling, or convection) and their effects can compound or confound one another. They affect the nucleation density and frequency as well as the ability of the bubbles to grow.

As discussed in an earlier section, dissolved gases are well known to impact boiling heat transfer. Several of the reviewed works specifically discussed degassing the water to improve experimental repeatability. Dissolved gases have the effect of lowering the boiling point. Since gas solubility is inversely related to temperature dissolved gases will begin to evolve at temperatures below the boiling point of water. The gas bubbles become nucleation sites for water vapor, lowering the activation energy needed to commence the phase change of boiling. The effect of gases is different depending on boiling regime. At low heat fluxes gases initiate nucleation and allow boiling to occur at relatively low wall superheat and so enhance heat transfer. However, at high or supersaturated concentrations, or at high heat fluxes the gases promote and stabilize film boiling dramatically. As has been mentioned earlier, this is the basis for the A729 process which uses water supersaturated with CO_2 to promote film boiling and control ingot butt curl [14].

Dissolved solids generally enhance heat transfer in the transition and nucleate boiling regimes. They are known to reduce vapor pressure in the solution, thereby increasing the boiling temperature. In the concentrations normally encountered in ingot casting cooling waters, the effect on vapor pressure and boiling temperature is very small. However, dissolved solids have a strong effect on nucleation site density.

The boiling heat flux is strongly dependent on the density of bubble nucleation sites [20]. This is to be expected since nucleation is a primary barrier to be overcome to initiate boiling. Jamialahmadi *et al* [15] found that in pool boiling, additions of inorganic salts initially decreased the heat transfer coefficient to a

minimum followed by an increase to a maximum and then more slowly decreased to an asymptotic value. The explanation for this observed behavior is the variation in nucleation sites over time. Solute concentrations near the liquid-vapor interface can increase several orders of magnitude during boiling [21]. This causes supersaturation and deposition. Since the interface tension between the water and the deposited solid is often lower than that between water and the aluminum ingot, the deposit is a preferred nucleation site. An increasing number of nucleation sites ensure that a larger fraction of coolant is in contact with the liquid/solid surface and more readily vaporize. Conditions that lower the energy required to nucleate vapor bubbles will decrease the superheat needed and will make boiling less homogeneous, i.e. more likely to undergo nucleate boiling rather than film boiling. Dissolved salts tend to increase the Leidenfrost temperature [13].

Suspended particles serve as nucleation sites for vapor bubbles. High levels of turbidity serve to promote film boiling in water without additions of CO₂ yielding a “hot” condition during the start of a drop. In cooling systems utilizing CO₂ for butt curl control, the particles have the opposite effect and in essentially “short circuit” the homogenous nucleation of bubbles so that the gas evolves before contacting the ingot. This makes the ingot butt “colder” and will lead to excessive curl, bleed-over and possibly starting cracks.

Surface roughness of an ingot affects heat transfer at several scales. Heavy lapping or liquation simply exposes greater surface area and changes the forced convective and free-falling flow of the cooling water. At a finer scale, asperities in the surface create pockets for nucleation of vapor bubbles. EMC, Wagstaff LHC™ and other methods that produce a very smooth surface are often more sensitive to variation in water chemistry and application than are DC methods. Alloys that tend to have different surface conditions behave very differently as well. For example, 5XXX alloys generally have rougher surfaces than 6XXX or 3XXX alloys. They tend to curl much more as well, perhaps because of the rougher surface. Oxides present on the surface are also seen to have dramatic effects on heat transfer. Small and large oxide patches can cause cracks themselves, and it is often seen that the steamline on an ingot butt is greatly impacted by the presence of oxide. This effect has been studied by others [25] [26] and is in itself worthy of a focused research effort, but beyond the scope of this paper.

Bubble growth is partially dependent on surface and interface tension. Because large bubbles decrease the surface area/volume ratio increased surface tension will drive the system toward larger and more stable bubbles. Large stable bubbles will have a greater tendency to escape to the surface and release the vapor to the atmosphere. In systems of lower surface tension, the bubble interface is less stable and growing bubbles will tend to break into smaller bubbles as they do not pay as great an energy penalty for the increased surface area. The smaller bubbles can then collapse in the bulk liquid, giving up the energy as the vapor recondenses and the surface energy is given back to the bulk. This will have the effect of increasing the temperature of the cooling water to a greater extent than a system in which the bubbles escape to the surrounding atmosphere.

Several researchers [7] [15] found that increasing dissolved solids reduced bubble coalescence under pool boiling conditions. However, Najibi *et al* [10] found that under flow boiling

conditions the concentration of dissolved solids did not affect bubble size because the bubbles were quickly detached from the surface.

According to Yu [2], the anionic and cationic contributions to boiling phenomena from dissolved solids are different from one another. Because water molecules are polar, they tend to be oriented at the liquid vapor interface such that the surface has a negative charge. A repulsive force is present between adjacent bubbles, but if the small repulsive force is overcome they are able to reduce the energy of the system through coalescence. Positively charged cations will be attracted to the negatively charged surface and thus serve to reinforce the repulsive force, inhibiting coalescence. Anions have the opposite effect, promoting coalescence and vapor film formation.

Surfactant effects on surface tension tend to inhibit bubble coalescence [7] but because they reduce the “rigidity” of the bubbles, more distortion can occur which increases the likelihood of contact and coalescence. The net effect is that they stabilize the steam film during under film boiling conditions [2].

Film boiling can occur under two different scenarios. In a system with a high Leidenfrost temperature a high degree of superheating at the interface is necessary. The high superheat creates such a large driving force that nucleation of vapor bubbles occurs at a very high density regardless of surface condition or cooling water composition. These bubbles are so uniformly and closely distributed at the high temperature interface that they easily contact, coalesce, and form a film. The other scenario can take place at a much lower superheat. In this case the vapor bubbles in a low surface tension solution nucleate heterogeneously, but distort or break up allowing them to coalesce into a thin steam film at a relatively low Leidenfrost temperature.

Solubility and reaction effects

Solubility of dissolved chemicals can have a significant influence on heat transfer in aluminum ingot casting. The solubility of gases decreases with increasing temperature and can therefore influence boiling. Most soluble solids increase in solubility (positive solubility) with increasing temperature although there are some notable exceptions in which solubility decreases with rising temperature (negative solubility [15]) [21].

In convective heat transfer the temperature gradient in the contacting fluid ensures that gases will tend to evolve nearest the high temperature interface. Solids that exhibit positive solubility will be farthest from the solubility limit at the ingot/water interface. On the other hand, negatively soluble solids will be closest to saturation and can potentially exceed solubility at the hot interface [21].

In boiling heat transfer, solute is rejected from the liquid at the interface. Under this condition local concentrations can increase dramatically, up to 4 orders of magnitude [15]. In the high flux boiling conditions which exist in the impingement zone of DC ingot casting, it is quite possible for solids with either positive or negative solubility to precipitate on the ingot surface. Evidence of this is often seen on and near the butt of an ingot as “steam stain”. Deposits are occasionally seen on the entire surface of the ingot, sometimes attributed to excessive levels of phosphate compounds

in the water. At other times a gold sheen on the ingots has been correlated with high iron concentration in the cooling water.

Deposition of solids on the ingot surface changes the wettability. Bernardin, *et al* [19] found that even monolayers deposited on an aluminum surface have a large effect on wetting behavior, bubble nucleation, growth and consequently, heat transfer. Jamialahmadi, *et al* [21] also found that specifically CaSO_4 deposits had a much lower interfacial energy with the solution than did the underlying metal. Because interfacial tension is so important to nucleation and growth of the vapor bubbles, the deposits have a profound effect on boiling heat transfer.

Sulfate and carbonate salts have widely varying solubility. Calcium sulfate (CaSO_4) has low solubility in water, inversely related to temperature. Sodium- and magnesium sulfate have somewhat higher solubility and are somewhat independent of temperature. The common carbonates and sulfates in order of ascending solubility are CaCO_3 , CaSO_4 , MgCO_3 , $\text{Ca}(\text{HCO}_3)_2$, NaHCO_3 , Na_2CO_3 , and MgSO_4 . In the formation of scales in water systems, it is generally the Ca^{2+} and Mg^{2+} ions that bear responsibility, while Na^+ is considered harmless [21]. In water softening processes, Ca^{2+} and Mg^{2+} ions are replaced by Na^+ to eliminate scaling. In some ingot casting operations it is likely that CaSO_4 , CaCO_3 , and MgCO_3 deposit on the ingot surface during the start of a drop, even though they may be later redissolved in the free-falling convection zone.

Najibi *et al* [10] reported that the solubility limit of CaSO_4 was increased with the addition of Na_2SO_4 during their experiments which led to a considerable increase in heat transfer. This supports the conclusion that in boiling, the local deposition of solids affects the heat transfer.

Another interesting chemical phenomenon was noted by Cui *et al* [7] which involved sodium bicarbonate, NaHCO_3 . At high temperatures in the nucleate boiling regime NaHCO_3 decomposes to CO_2 and Na_2CO_3 . In a 1% solution of NaHCO_3 it was estimated that an equivalent of 0.0094 scf/gallon CO_2 may evolve. At concentrations present in ingot cooling water systems, the quantity is much less, and while it is unlikely to contribute significantly to variation in heat transfer, it is a question that warrants further investigation and confirmation.

Summary and Conclusions

The water chemistry investigations conducted were based on the long-held belief that alkalinity, hardness, pH, conductivity, and turbidity were the major influences on heat transfer variation in aluminum fabrication ingot casting. Toward that end, a simple array of chemicals was used to dope the water to the desired composition. Sodium bicarbonate (NaHCO_3), calcium chloride (CaCl_2), and magnesium chloride (MgCl_2) were used for attaining alkalinity, calcium hardness, and magnesium hardness, respectively. These are not the natural contributors to alkalinity and hardness in the typical sources of ingot cooling makeup water.

The natural sources of alkalinity and hardness are calcite (CaCO_3), and dolomite ($\text{CaMg}(\text{CO}_3)_2$). Some sources of makeup water contain little sodium, which has been shown to affect solubility of the other species and other heat transfer phenomena in boiling. However, during the winter and early spring months in

locations which draw makeup water from surface water sources, NaCl concentration can spike as runoff from snow melt enters the river. Other facilities introduce Na^+ and removes Mg^{2+} and Ca^{2+} as it softens its makeup water supplied by the municipal water supply. Still others draw from wells, each with a distinct composition. Some well water is quite high in sulfates (SO_4^{2-}) most likely from local gypsum deposits in the ground.

Additives for corrosion inhibition, microbiological control, turbidity control, and other purposes have been found to have an impact on heat transfer in the ingot casting process and some are now maintained at levels primarily targeted to ensure water quenchability is stable.

The understanding of the effects of cooling water composition is not complete. It appears in hindsight that some of the parameters historically chosen for control of ingot quenching have been a matter of convenience, because simple and effective measurement techniques existed for these variables. The axiom "You can only control what you can measure" has often been the philosophy applied to our ingot plant cooling water systems.

The expanded literature review presented in this report has broadened the understanding of possible mechanisms affecting heat transfer in ingot casting operations. More remains to be done to develop the capability to accurately measure, quantify and model heat transfer in the ingot casting process. Thorough understanding of this subject will provide a mechanism for improved process control, improved recovery, and safer ingot plants.

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