

Light Metals 2015

ALUMINUM PROCESSING

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Light Metals 2015

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Session I

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PRIORITIZING WATER CONTAMINANTS' IMPACT ON HEAT TRANSFER IN CASTING ALUMINUM INGOTS

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Keywords: heat transfer, heat transfer coefficient, cooling rate, quench, aluminum, ingot, casting

Abstract

The impact that various water treatment additives and contaminants might have on aluminum ingot casting heat transfer was evaluated using laboratory heat transfer measurements simulating ingot quench waters. These included: oil in water, corrosion inhibitors and various dissolved solids. Test samples were prepared and submitted as blind samples for heat transfer and cooling rate studies to the Center for Heat Treating Excellence at Worcester Polytechnic Institute. Demineralized water was used as a baseline for comparison to waters containing either additives or contaminants. Heat transfer (BTU·s/ft² hour °F) and Cooling Rate (°F / sec) over a range of 900°F to 150°F was measured. The heat transfer curves captured the entire boiling range from film, through nucleate to convection. Changes in heat transfer or cooling were plotted against the baseline as well as untreated supply water. The results from this work were used to help prioritize maintenance and operational practices at an industrial casting plant and to minimize shifts in heat transfer caused by previously unmonitored water components.

Introduction

Most ingot casting water influences are well understood [1, 2]. This study looked beyond the common indicators to identify chemistry or physical factors that may impact aluminum casting heat transfer and cooling rate as the process moves through the

three phases of heat transfer along an ingot surface: film boiling, nucleate boiling and convection cooling, collectively referred to as “quench.” [3]

Industrial data was collected showing the variations in casting water chemistry during the period of this study (November 2012 through February 2013), a summary of which is shown in Table 1. Toly triazole, zinc, ortho phosphate and organic phosphate values are provided by the corrosion protection program. Sulfate and chloride are primarily from the well water but also from alkalinity adjustment (sulfuric acid) and microbiological control (sodium hypochlorite). Casting process key process indicators (KPI) for water are turbidity, temperature, alkalinity and total hardness. Good process control of these variables yields an acceptable water “quality” for casting.

Of special interest were the variations in sulfate and chloride concentrations due to management of the incoming water from a deep well field at the water plant. There are six ground water wells deep enough to not be influenced by surface water. Analysis of these wells showed that they were not uniform in hardness, alkalinity, sulfates and chlorides, so a matrix was provided to the water plant management to allow them to match wells to minimize swings in chemistry. This matrix was not always followed. Over a period of a few days, sulfate could swing by as much as 75 PPM (25%), while chloride shift might change by 40 PPM (50%). The variation is shown in Figure 1.

Table I. Casting Water Quality Measurement

Date	TTA	Zinc	O-PO4	Org-PO4	TURB	TEMP	HRD	ALK	Sulfate	Chloride
	Inhibitors				Key Operating Indicators				Well changes	
MIN	0.90	0.41	0.02	3.20	0.2	70.6	359	70.5	211.50	24.20
MAX	4.20	0.81	1.08	31.70	4.2	79.7	382	80.5	330.00	113.00
% IN					98%	99.9%	100.0%	99.9%		
% OUT					2%	0.2%	0.0%	0.1%		
% > UCL					2%	0.0%	0.0%	0%		
% < LCL					0%	0%	0.0%	0%		
Mean	2.08	0.58	0.48	20.76	1.0	77.8	370	75.0	305.87	70.31
SD	0.56	0.07	0.11	3.94	0.5	0.7	2.7	1.2	21.16	15.23
ppk					n/a	2.4	1.8	1.4		

Note: All values in parts per million (ppm) except turbidity (NTU) and Temperature (°F)
 TTA – toly triazole. O-PO4 – ortho phosphate. Org-PO4 – organic phosphate.

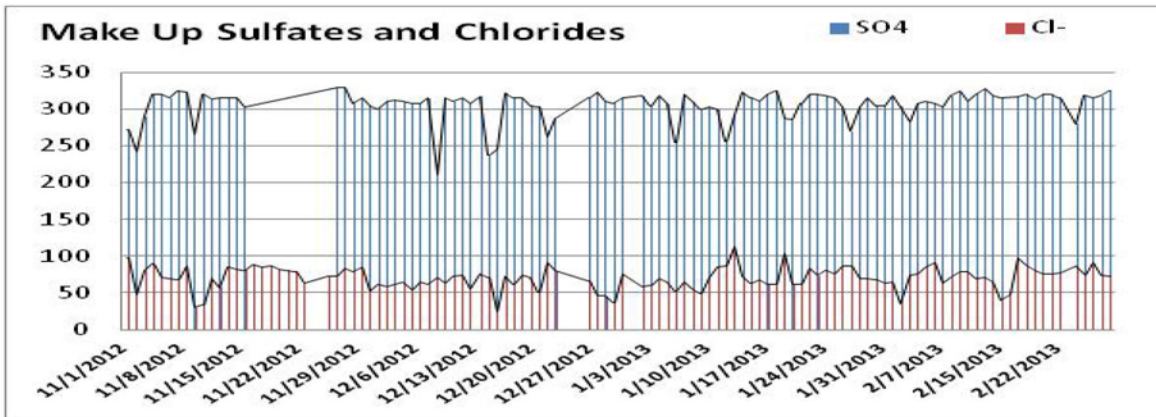


Figure 1. Variation in incoming water sulfate and chloride (ppm).

Next, select variables were further subjected to heat transfer and cooling rates studies using a common aluminum alloy as a test piece as described in the method section below. Make up waters were submitted as blind samples to a contract lab for analysis and the results of 5 tests runs were collected for each water.

The basic goals of the study were all related to impact on heat transfer:

1. Impact of source water vs. RO water.
2. Impact of corrosion and scale inhibitors added to the water.
3. Impact of variations in the source water quality due to well field management.
4. Impact of contaminants added inadvertently to the water.

Methods

Make up test waters were prepared at the Solenis Customer Applications Laboratory, Wilmington, DE to explore the following variables:

1. Potential impact on heat transfer of the corrosion inhibitors in use. An organic phosphate and a zinc chloride inhibitor have been in use since 2002 at the target industrial site. The addition of an aromaticazole inhibitor is more recent.

2. Potential impact on heat transfer with changes in water conductivity driven by variation in sulfate and chloride concentration.
3. Potential impact on heat transfer related to source water compared to pure reverse osmosis (RO)/demineralized water.
4. Potential impact on heat transfer of common contaminants such as oil in water.

Blind samples were prepared and shipped to the contract laboratory for heat transfer and cooling rate determination as described in the table below. Other traditional casting quench constituents and parameters were not evaluated (water temperature, hardness and alkalinity [2]) since the existing casting water process operates at a level of control greater than 5-Sigma, often well above 6-Sigma. In short, the process variable needs to be centered within the specification limits with a calculated standard deviation (SD) small enough to include three SD fractions between the mean and the specification limit (upper or lower). [5] Table 2 provides the target water chemistry parameters for all lab prepared blind samples.

Table II. Water chemistry submitted for testing.

PRIORITY	RUN	Water			Chemistry as Product			Chemistry as Actives			WPI INFO			NOTES	
		Low Cond	Std Cond	High Cond	11-719 ppm	MS 995 ppm	11-166 ppm	11-719 ppm as Actives	MS 995 ppm as Zn	11-166 ppm as TTA.Na	Comp 1	Comp 2	Comp 3		
1	1	DI Water			---	---	---	---	---	---	---	---	---	---	DI Water Blank
2	2	---	X	---	0.0	0.0	0.0	0.0	0.0	0.0	---	---	---	---	Std Conductivity Blank
3	3	---	X	---	20.0	2.5	0.0	8.0	0.6	0.0	X	X	---	---	Std Conductivity - Benchmark Treat / DoE
4	4	---	X	---	20.0	2.5	6.0	8.0	0.6	3.0	X	X	X	---	Std Conductivity - New Treatment / DoE
5	5	X	---	---	20.0	2.5	6.0	8.0	0.6	3.0	X	X	X	---	Low Conductivity - New Treatment
6	6	---	---	X	20.0	2.5	6.0	8.0	0.6	3.0	X	X	X	---	High Conductivity - New Treatment
7	7	---	X	---	20.0	0.0	6.0	8.0	0.0	3.0	X	---	X	---	Std Conductivity - Additive DoE
8	8	---	X	---	20.0	0.0	0.0	8.0	0.0	0.0	X	---	---	---	Std Conductivity - Additive DoE
9	9	---	X	---	0.0	2.5	6.0	0.0	0.6	3.0	---	X	X	---	Std Conductivity - Additive DoE
10	10	---	X	---	0.0	2.5	0.0	0.0	0.6	0.0	---	X	---	---	Std Conductivity - Additive DoE
11	11	---	X	---	0.0	0.0	6.0	0.0	0.0	3.0	---	---	X	---	Std Conductivity - Additive DoE
12	12	---	X	---	20.0	2.5	6.0	8.0	0.6	3.0	X	X	X	---	Run 4 + 3 ppm Hydraulic Fluid
13	13	---	X	---	20.0	2.5	6.0	8.0	0.6	3.0	X	X	X	---	Run 4 + 3 ppm Comp 4

Deionized water was used as the baseline water (DI) and represents ultrapure waters such as RO water used at some industrial locations for makeup. The Standard Conductivity blank is the normal well water make up for this process minus any additives. The table shows the order of testing for the blind samples.

Determination of Heat Transfer and Cooling Rates

Solenis contracted with the Center for Heat Treating Excellence at Worcester Polytechnic Institute for the heat transfer and cooling rate studies. WPI’s CHTE is a university based research facility specializing in such work for government, aerospace, and industry. The full process is explained in Mohammed Maniruzzaman’s “Quenching – Understanding, Controlling and Optimizing the Process” available from the WPI-CHTE. In brief the process involves heating a sample cylindrical probe of the alloy in question (51xx series aluminum) under tightly controlled circumstances and then quenching the billet with the water provided by Solenis. The process is repeated 5 times and an average of heat transfer and cooling rates for each water is determined by a proprietary process. [6]. A drawing of the device employed is shown in Figure 2.

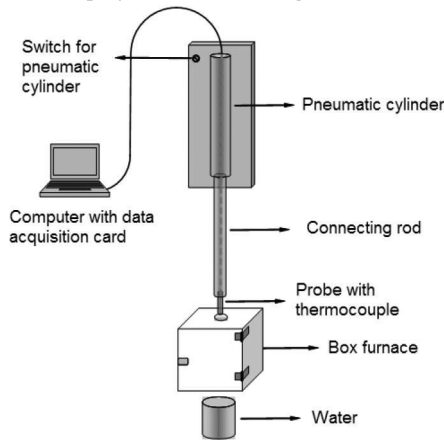


Figure 2. WPI-CHTE device for measuring heat transfer and cooling rate.

The size and geometry of the alloy billet is carefully controlled to avoid thermal gradients that might interfere with heat transfer to the internal thermocouple (k type) gathering the heat change information. The resulting data is then presented as graphs showing the process of quenching from film boiling through transition to nucleate boiling (maximum transfer) to convection cooling in Figure 3 [6]. The summary curves are shown in Figures 4 and 5 and are examined in the next section.

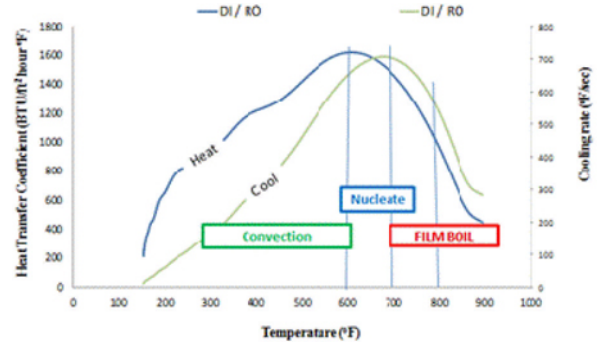


Figure 3. Heat Transfer and Cooling Rate curves showing film to convection transfer.

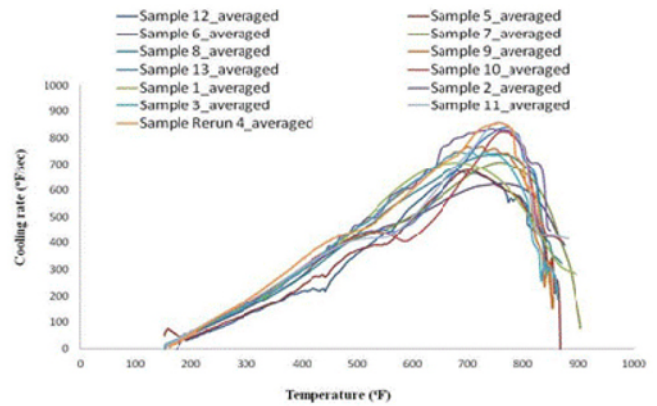


Figure 4. Cooling Rate curves (averaged) for sample water.

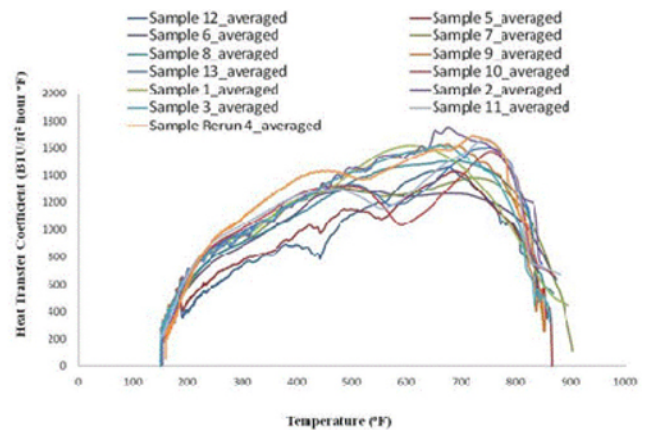


Figure 5. Heat Transfer Rate curves (averaged) for sample water.

Results

Water vs. Source Water

Because source water quality can be controlled via treatment, heat transfer and cooling rate curves representing the standard source water condition were compared with a highly purified (Deionized water - DI) make-up water as a baseline. Source water quality improvements can be made commercially in a variety of ways including installation of a reverse osmosis (RO) system or Deionizer/Demineralizer (DI) depending on the allowable level of contaminants for the process. In Figure 6 the cooling rate and quench heat transfer rate, Figure 7, compares DI and the standard condition for untreated source water.

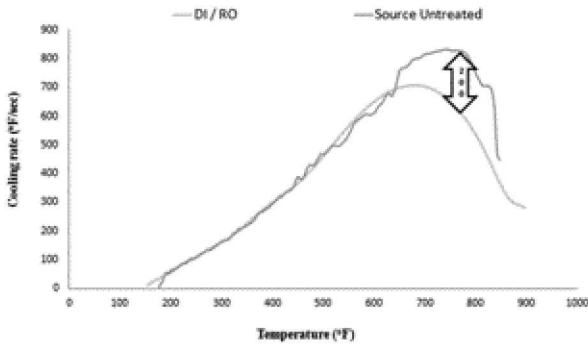


Figure 6. Cooling rate for DI and source (well) water

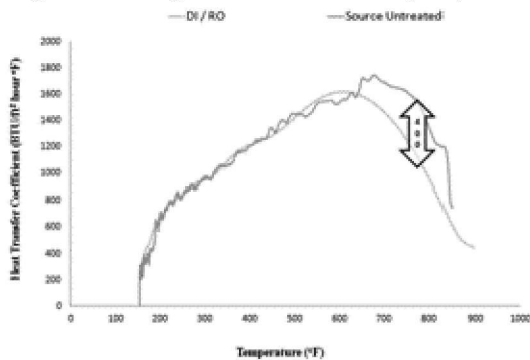


Figure 7. Heat transfer results for DI and source (well) water

The primary difference between the two waters is in the film to nucleate boiling stage and is likely driven by the dissolved solids

in the water creating bubble nucleation sites for improved heat transfer or inhibiting film bubble coalescence [2, 4].

Water vs. Conductivity

Figure 8 shows an average of 6 months sampling along the six wells that make up the potable water supply for the commercial facility. Each well was tested at least 8 times. Sulfates (blue) range from 55 ppm on the South end to 225 ppm on the North. The middle wells seem to have more chlorides (red) than the ones on either end. Ranging from 25 to 50 ppm; testing is ongoing.

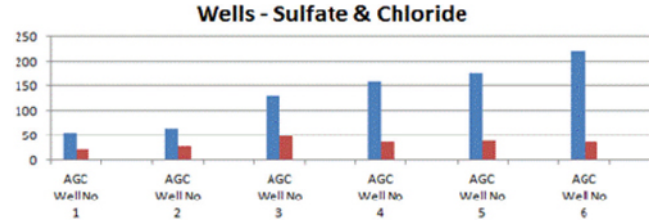


Figure 8. Average influent water variability (ppm) among 6 wells during 6 month period

Because alkalinity and total hardness are well controlled within tight specification limits in the casting water system, alkalinity by using acid addition with on line analyzers and hardness by blow-down of cycled water replaced by low conductivity make up, the major variable in water conductivity becomes the amount of sulfates and chlorides. To determine their impact on casting, treated sample water was modified for low and high conductivity by diluting the treated sample water with DI/RO water to yield a low conductivity (400 to 500 uS) water and by adding sulfate to achieve a high conductivity (1400-1500 us) water. Table 3 shows the make-up of the high and low conductivity water.

Figures 9 and 10 compare the cooling rate and heat transfer curves for high and low conductivity casting water. Both high and low conductivity waters, driven primarily by sulfates and chlorides, suppress heat transfer. Both are a significant departure from the normal operating curve, especially during the critical nucleate boiling stage.

Table III. Chemical parameters for various test waters

Component	Units	Low Conductivity Water	Std Conductivity Water	High Conductivity Water
Conductivity	µs/cm	400-500	900-950	1400-1500
pH		8.0	8.0	8.0
Alkalinity total, (as CaCO ₃)	mg/l	85	75	75
Chlorides, (as Cl)	mg/l	27	60	60
Sulfates, (as SO ₄)	mg/l	75	298	620
Calcium, as (as CaCO ₃)	mg/l	10	276	276
Magnesium, (as CaCO ₃)	mg/l	5	99	99
Silica, (as SiO ₂)	mg/l	9	12	12

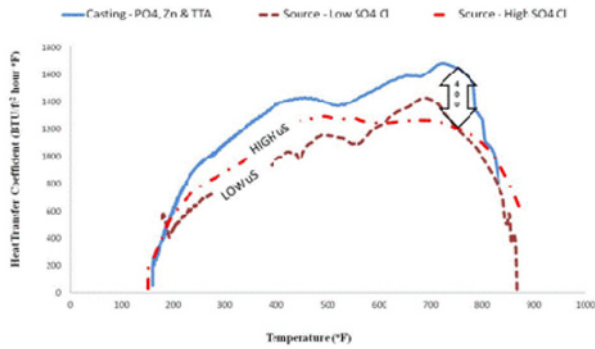


Figure 9. Heat transfer rate curves showing impact of conductivity

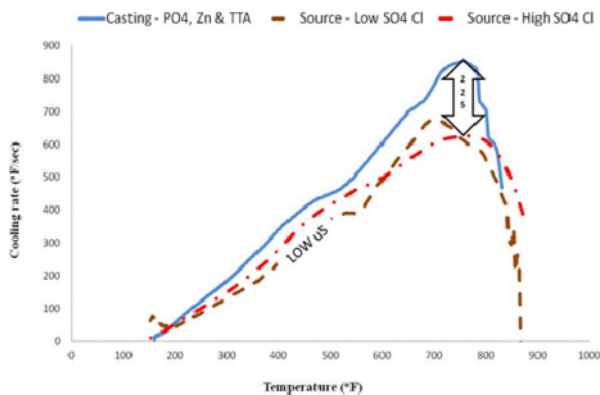


Figure 10. Heat transfer and cooling rate curves showing impact of conductivity

Water vs. Inhibitors

This commercial casting water system has employed a two part corrosion inhibition system for the past decade utilizing an organic phosphate and zinc supplement. The casting water recipe calls for low alkalinity and high total hardness which has resulted in aggressive corrosion of the aluminum bodies of the casting molds at the site. Bench studies showed that an aromatic azole type inhibitor would control corrosion under mill conditions. When this additive was first deployed in 2005 and 2006, the mill experienced issues with casting quench stability that were attributed to the azole additive. One reason for this study was to test that hypothesis.

Source water was treated with the target level of each inhibitor to first identify their individual roles in changing the quench profile. Figure 11 shows the individual chemical contributions to heat transfer change, Figure 12 combines all into one casting water. As can be seen in figure 10, the organic phosphate curve (PO4) is similar to the source water curve. The addition of zinc and azole had a more significant, yet similar, impact in the critical nucleate boiling zone. In the case of the zinc, losing 450 BTU's per square foot per hour or 32%.

However, when combined at operating levels (Figure 12), the sum was similar to untreated source water, again pointing out the necessity for tight control of the individual process chemical residuals in the casting water to minimize shifts in casting heat transfer / quench. Cooling rate curves were similar.

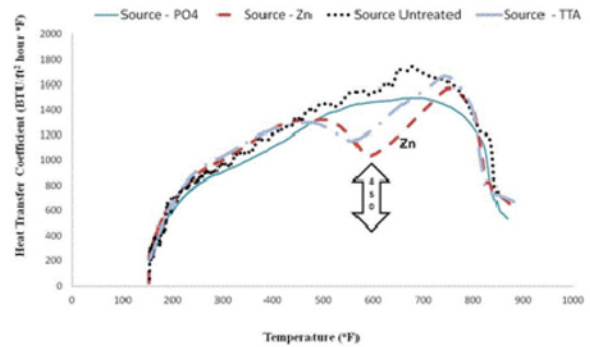


Figure 11. Heat transfer curves showing chemical impact

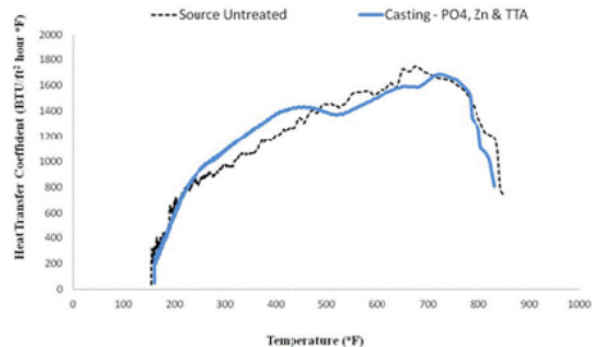


Figure 12. Heat transfer curves showing combined chemical impact

Water and Oil

Many commercial ingot casting facilities have issues with oil contamination of the quench water, normally associated with casting mold release agents. This particular location uses no casting mold lubricant but has a history of tramp oil additions to the casting water. In discussions with the maintenance engineer responsible for the casting system, it was learned that the platen hydraulic system which supports the cast ingots can use 30 to 300 gallons of neat hydraulic fluid in a month, depending on how well the gland seal is holding. The hydraulic fluid is made down with demineralized water into a 5% oil in water emulsion. In addition, leaks from other hydraulic components from various minor casting pit equipment add their contribution. Large oil losses are usually associated with observations of an increase in floating foam on the system cooling tower basins. Historically 3 ppm of oil in the casting water has been considered of minor concern to casting success. To determine oil-in-water's role in quench, 3 PPM of platen hydraulic fluid, provided by the plant, was added to casting water. The exact type of fluid was not disclosed per an existing non-disclosure agreement. Heat

transfer and cooling rate curves were recovered and are shown in figures 13 and 14. As the casting water cools from film to transitional boiling the heat transfer rate decreases by 500 BTU per unit or 31%. The difference decreases to 200 BTUs (12%) as nucleate boiling transitions to convection but increases again to 700 BTU per unit or 43% during convection heat transfer.

The impact on cooling rate was most pronounced during the transition to nucleate boiling stage (800°F to 500 °F per second or 38%). It is easy to see that variations in oil contamination could play a significant role in quench shifts during cast initiation when a stable, predictable transition to nucleate boiling is important.

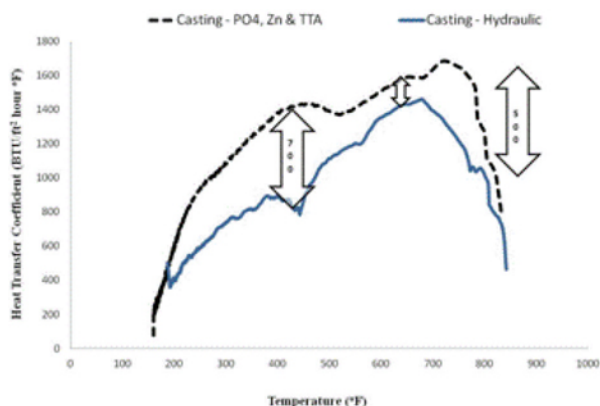


Figure 13. Heat transfer curves showing hydraulic oil impact

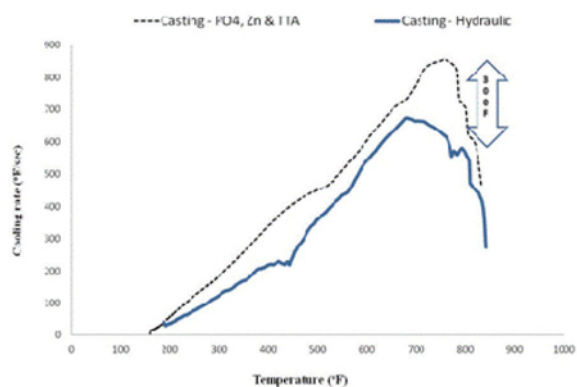


Figure 14. Cooling Rate curves showing hydraulic oil impact

Summary

This work demonstrates that variation in makeup water quality along with the use of various corrosion control agents have either no significant impact on quench rate variation or small impacts. In contrast, the magnitude of the impact on heat transfer and cooling rate (quench) of small amounts of oil in the water ranked as the highest concern.

The addition of the azole corrosion inhibitor ranked second as a concern, due to the significant change in the heat transfer curve

when it is employed. While the azole is superior for corrosion control its impact on quench variability may be a factor when considering its use. Unlike tramp oil, the inhibitor can be carefully metered and its impact on quench made predictable. The benefit it provides in corrosion control is expected to override any concerns related to quench variability.

The highly variable chloride and sulfate fraction of the source water also ranked as a concern, though the impact of both high and low conductivity samples, modulated by raising both constituents, seemed to have the same impact. At the commercial site this work helped in the updating of an existing well management program for the water plant.

Acknowledgements

I would like to thank the contributors who assisted with this project. Bill Carey, John Gast, Steve Wood, Tim Patterson, Daniel Dole, Michael Todd, and Jamie Doran- Solenis Wilmington (Delaware) Research Center. Charlie Angle and Dwight Emerich --Solenis Applications Staff. Also Dr. Richard Sisson, Jr. and the staff at The Center for Heat Treating Excellence, Worcester Polytechnic Institute.

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