THE SAFE AND EFFICIENT WAY OF COOLING: ILTEC – IONIC LIQUID COOLING TECHNOLOGY

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ABSTRACT

More intense furnace operations require effective cooling in order to achieve low refractory wear and good furnace lifetimes, making cooling technology an important aspect of furnace operations. However, the use of water – today's standard cooling medium – has some disadvantages, as it can cause problems both during furnace start up and operation, namely hydration problems, corrosion, and explosions. Furthermore, the energy which is lost by extensive water cooling cannot be used anymore and is normally lost.

With METTOP's new patented cooling technology it is possible to overcome the disadvantages of water by using an alternative cooling medium, namely ionic liquids (ILs). The big advantage of ILs is the fact that they can be used at higher temperatures than water (up to 200 °C), as well as they do not cause explosions when contacting molten metal or slag. This results in a longer refractory and cooling element lifetime and – as one of the biggest advantages – in a very safe operation.

The present paper explains the details of this new development and gives an overview about possible applications where the Ionic Liquid Cooling Technology utilizes its strengths. Special attention has to be paid to an easy industrial realization and new possibilities of cooling.

KEYWORDS: *Furnace integrity, cooling, ionic liquids, safety.*

1. INTRODUCTION

The modern metallurgical industry faces numerous challenges – one is the necessity of achieving a high process intensity and productivity. As a result, the increased load of all metallurgical vessels results in the need of a state-of-the-art furnace and refractory design. Cooling systems extend refractory and furnace lifetime by lowering the temperature within the refractory and protecting the steel construction of highly stressed furnace areas [1-5].

In dependence of the installed system, the heat transfer can be set. Copper elements with water-cooling inside the furnace wall – as they are often used in flash furnaces and electric furnaces – are very effective; 100,000 W/m² is a typical value for this type of cooling. However, water cooled panels inside the furnace wall are critical in respect of process and work safety; leakages can result in severe explosions.

An important aspect for water-cooling elements is the overall and cooling channel design. A diligent design work guarantees effective cooling. The cooling channels can be either drilled or cast-in. The disadvantages of drilled channels are the drilling effort and problems with tightness, as well as the limited geometry (e.g. curvatures are not possible). Cast-in pipes can be made of copper, monel, or coated copper (nickel or silver). When using cast-in pipes, it is essential to avoid a gap formation between the pipe and the surrounding Cu element during the casting (and cooling) of the copper element. Furthermore, a good contact between the cooling element and the refractories is important to ensure a good heat transfer. Air gaps between refractories and cooling element can occur during operation and due to the thermal cycles. Therefore, special cooling element designs were developed. One example is the Composite Furnace Module (CFM [6]; figure 1), where fingers should guarantee the contact and provide a homogeneous hot face temperature with a high temperature gradient. A so called freeze lining by forming a solid layer on the refractory surface can be achieved when using CFM cooling elements.

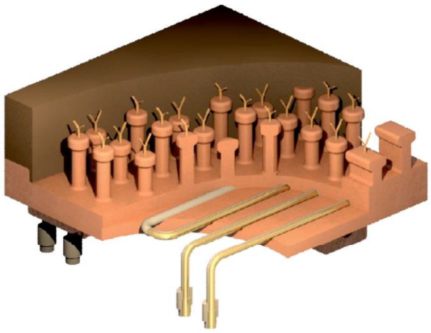

Figure 1: Example for a CFM cooling element

Generally and independent of the type of cooling system which used, the whole furnace construction has to be considered: To achieve optimum results, namely effective cooling, good refractory protection, and long furnace campaigns, a harmonic design of refractory and cooling system is required.

2. DISADVANTAGES OF WATER COOLING

Problems with water-cooling can arise both during heat up of the furnace and operation. Main cause is the medium water itself, as well as the excessively strong cooling effect.

When heating up the vessel, the residual water from the refractories evaporates. Hydration of MgO containing refractories takes place in the temperature range between 40 and 180 °C; therefore, the temperature during furnace heat up should be increased rapidly up to 200 °C. The hydration reaction from periclase (MgO) to brucite ($Mg(OH)_2$) is associated with a volume increase of up to 115%. As a result, refractory damages occur – ranging from cracks to the total destruction of the bricks; this can also result in damages in the furnace structure. Even with a rapid temperature increase, hydration problems are likely to occur in the regions near the cooling elements, as due to the low temperature of the cooling water (< 100 °C) and the resulting strong cooling, the temperature of the cooling elements is significantly lower than in the other parts of the furnace. Consequently, condensation of water – evaporating from the refractories – preferably occurs in the areas next to the cooling elements, leading to hydration and associated damages.

During operation, the main problems with water are leakages: This can result in the mentioned hydration when contacting the refractories. A major problem is the hazard of explosions and severe damages when water contacts the liquid metal. These explosions are an issue regarding work safety, but also a significant economic aspect: A standstill causes a tremendous financial loss. Common practice to avoid such leakages is stopping the furnace campaign early, with still a sufficient amount of refractory material remaining. However, also this method results in additional, unnecessary costs, as a certain amount of refractories is replaced before time.

Usually, water cooled elements are supplied by a high volume flow due to safety reasons. Therefore, the cooling effect is very strong and the cooling element surface is cold. At water cooled tap holes this strong cooling effect can result in SO_2 formation and splashing – and therefore in reduced work safety. A further negative effect of the intense cooling is dew point corrosion (wet corrosion); due to condensation of flue gasses – containing corrosive compounds like H_2O, SO_3, NO_x, and HCl – on the cooling element. This occurs if the cooler surface temperature drops below the respective dew point. Dew points of 150 to 250 °C are typical for sulphuric acid and depend on the SO_3 and moisture content [7, 8]. SO_3 is formed from SO_2; this is controlled by thermodynamics and kinetics and has its optimum formation temperature at about 600 °C. The consequences are damages of the cooling elements and leakages. This is an important and dangerous effect at blank copper cooling elements without an additional protective refractory layer. Examples are water cooled electrodes and cooling frames in the offgas area. A further corrosion effect occurs if NO_x or chlorides form the corresponding acid (nitric acid and hydrochloric acid) [7, 8]. Wet corrosion also occurs as a result of erosion. As erosion removes copper material, the cooling channels get closer and closer to the surface of the element. As a result, the surface temperature of the cooling element decreases until it reaches the dew point for acid condensation [9].

Water cooling also means a certain removal of heat. However, the temperature level is too low for the production of electrical energy. High pressure systems may overcome this problem – however they are vulnerable for mechanical damages and cannot be used in many applications. Also when cooling small and critical areas, the installation of a steam generator is not feasible and the heat is lost and wasted.

When regarding cooling applications in metallurgy, the temperatures could be much higher as they are when using water as a cooling medium. For example, a temperature of some hundred degrees would be still sufficient for an increased refractory and vessel lifetime. However, this would avoid the above mentioned problems, for example the dew point corrosion.

3. IONIC LIQUIDS AS AN ALTERNATIVE COOLING MEDIUM

To overcome the above mentioned disadvantages of water as cooling medium, an alternative is necessary. Solution and perfect cooling medium, respectively, is a salt with a wide liquidus range and a low melting point – namely an ionic liquid (IL). Per definition, ionic liquids show a melting point below 100 °C; many of them are liquid even at room temperature, caused by their badly coordinated ions. As their name suggests, ILs consist only of ions. Dislocated charging and one ion based on an organic molecule avoid the formation of a stable crystal lattice, so that only a minor amount of thermal energy is required to conquer the lattice energy and break the crystal lattice [10]. Varying the cations and anions allows designing ILs with different properties (e.g. melting point, viscosity, and solubility). The cation type is significant for the identification. Increasing the size of anions or cations causes a reduction of the melting point. Furthermore, the geometry of the cation influences the melting point, namely symmetric cations like 1,3-dialkyl have a higher melting point compared to asymmetric ones [11].

Ionic liquids have a variety of properties which give them unique character; some of them make them suitable and perfect for the use as a cooling medium [12]:

- Non flammable
- High ionic conductivity
- Wide temperature range for liquid phase
- Large electrochemical window
- Practically no vapour pressure below decomposition temperature
- Relatively low viscosity

Generally, ionic liquids are viscous compared to molecular solvents and also have a higher density than water. The strength of their heteroatom-carbon bonds and their heteroatom-hydrogen bonds respectively, indicates their thermal stability. An exceptionally considerable character of ILs is the fact that they have no measureable vapour pressure (i.e. negligible values). The heat capacity of ILs only shows existing, but relatively weak temperature dependence over a temperature range between -50 and 300 °C. The thermal conductivity, which is an important property for heat transfer applications, is significantly affected by water contamination [11, 13, 14].

Using ILs as cooling medium allows higher inlet and outlet temperatures than with water. Furthermore, an adjustable intensity of cooling is possible, also during heating up. The high cooling element temperature prevents the condensation of water vapour and – as a result – minimizes the risk of refractory hydration during heating up or due to leakages. A sufficient high cooling element surface temperature avoids the formation of corrosive compounds, and dew point corrosion respectively. Furthermore, heat or energy recovery gets feasible if the cooling medium temperature is higher. Ionic liquids decompose above a certain temperature under formation of gaseous components. As a result of the aforementioned aspects, using ILs as a cooling medium is a save alternative to water and allows cooling new areas with the following economical and technical advantages:

- No hydration due to strong cooling
- No hydration due to leakage
- No explosions due to leakage
- No dew point corrosion problems
- Adjustable cooling
- New possibilities for application of cooling
- Energy recovery (reducing CO_2 certificates)

4. METTOP'S IONIC LIQUID ISIS B

ISIS B is a special selection of anions and cations determining the characteristics of the ionic liquid. Furthermore, special additives influence these characteristics, for example lower the melting point in order to be liquid near or at room temperature. The ionic liquid ISIS B, which is perfectly suitable as a cooling medium in metallurgical furnaces shows the following basic properties:

- Melting point: below room temperature
- Short term stability: 400 °C
- Long term stability: 200 °C
- Density: 1.28 g/dm^3 (20 °C); 1.25 g/dm^3 (65 °C)
- Heat capacity: 1.5 – 1.6 J/gK (30 – 100 °C)
- Viscosity: 50 mPas (20 °C); 8.5 mPas (90 °C)

An essential characteristic of METTOP's ISIS B is its chemical composition. A special and patented production process ensures that this ionic liquid is free of chlorine. The possibility of using ISIS B with every conventional cooling element material and most of the common sealing materials is a result of this characteristic.

Based on these values, ISIS B can be used in a temperature range between 50 and 200 °C, in order to guarantee a suitable viscosity for pumping, as well as to use it for a long time as non consumable in a closed circuit. The thermal properties are worse than water – however the temperature difference between inlet and outlet can be up to 150 °C. Therefore, a proper cooling element design allows the same or even a higher heat removal when using ISIS B instead of water.

When contacting liquid metal (above 400 °C), ISIS B decomposes under forming a flame (www.mettop.com; movie ISIS B). Although the ionic liquid contains a certain amount of fluorine, no hydrofluoric acid formation can be detected. If a leakage occurs below bath level, the gaseous decomposition products form bubbles and escape through the bath surface. This effect results in a certain splashing inside the metallurgical vessel. However, no reaction between decomposition products and liquid metal or slag occurs. Furthermore, there is no H_2 formation and resulting explosion possible. Another big advantage is the non flammable behaviour of ISIS B. This means, as soon as the heat source is removed, the decomposition stops immediately. In case of overheating without contacting liquid metal or slag, ISIS B will also decompose and form gaseous components. However, there is no solid residual which may block the cooling circuit. An overpressure valve, and vent respectively, allows the decomposition products to escape.

Generally, handling ISIS B is easy, but needs some special care. The ionic liquid is hygroscopic; this means it will absorb moisture from the air which should be avoided. Especially at higher temperatures, oxygen reacts with the ionic liquid which results in an aging and in the necessity of replacing it. In order to prevent both moisture and oxygen contact, ISIS B should be operated in a closed circuit and covered with nitrogen if there is a plain surface.

The following table 1 summarizes the properties and behaviour of the possible cooling media water, thermal oil and the ionic liquid ISIS B. The two main disadvantages of thermal oil are its flammable behaviour – once ignited thermal oil burns autonomously – as well as the formation of a solid residue in case of overheating a cooling element – this means a cooling circuit cannot be restarted after a longer shut down.

Table 1: Characteristics and comparison of used cooling media for the metallurgical industry

	Water	**Thermal oil**	**Ionic liquid ISIS B**	**ISIS B/ water**	**ISIS B/ thermal oil**
Medium temperature	5 – ***60*** °C	5 – 300+ °C	(20) 50 – 200 °C	++	0
Usual temperature difference	5 – ***15*** °C	5 – 250 °C	5 – 150 °C	++	0
Overheating	vaporization	pyrolysis, ***solid*** and gaseous components	decomposition, gaseous components	+	++
Contact with liquid metal	vaporization, ***reaction, explosion***	incineration, gaseous components	decomposition, gaseous components	++	+
Flammable	no	***yes***	no	0	++

5. APPLICATIONS IN METALLURGICAL FURNACES

Modern lining designs in copper producing vessels require new technologies in order to reduce operation costs, increase the furnace availability and increase the safety conditions. To achieve and guarantee these targets, the ionic liquid cooling technology was developed. Due to the special properties and resulting advantages over conventional water cooled elements, also critical sections of metallurgical vessels can be cooled without safety issues. The primary idea of ILTEC is not to substitute all water cooled areas – nevertheless this would be possible – but introducing this technology for areas where water cooling is risky as well as where hydration or corrosion effects can be observed.

Construction, design, and calculation of cooling elements and the necessary cooling circuits using ionic liquids as cooling medium is done customer tailored, but in a similar way to the current procedure for water cooled elements. Although conventionally water cooled copper elements can be operated with ISIS B, an adjusted design will improve the situation. Together with an optimized design of the surrounding refractory, CFD calculations help to find the best solution for a critical furnace area.

There is a wide range of application possibilities in metallurgical furnaces for the ionic liquid cooling technology. Generally, two fields need to be defined:

- Substitution of water in critical areas or where corrosion and/or hydration problems occur
  - Tap hole (figure 2)
  - Furnace roof
  - Offgas junction
  - Anode furnace mouth
  - etc.
- Totally new application where cooling with water is not possible or too risky
  - Furnace bottom and sidewall (below bath level)
  - Tuyeree zone
  - Purging plug
  - TSL lance tip (figure 2)
  - Measurement lances
  - etc.

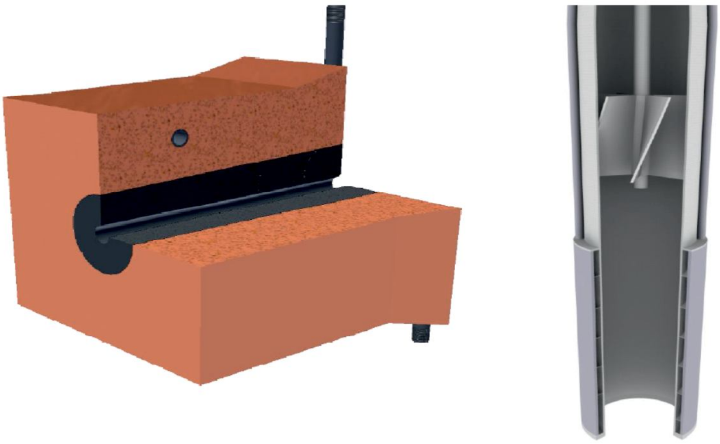

Figure 2: Tap hole and TSL lance tip, designed for being cooled with ISIS B

6. ILTEC SYSTEM

A fundamental characteristic of ILTEC is to use a closed circuit for the ionic liquid – the primary cooling circuit. Reason for this realization is to make ISIS B not a consumable. Tank, circulation pump and heat exchanger are the heart of every system, while the instrumentation, redundancy and size need to be tailored for each application in order to minimize the costs and maximize safety and functionality. Figure 3 shows an example of an ILTEC system which was developed and built for one medium sized cooling element and removing up to 100 kW of thermal energy.

As mentioned before, the idea of ILTEC is not substituting water completely. However, it may be useful to combine some bigger areas in order to make use of the energy removed from the vessels. While the temperature difference is much too low in case of water, a difference of 150 °C allows utilizing the waste heat or generating electrical energy.

Calculations show that a thermal input of approximately six Megawatts is necessary in order to allow power generation under economical aspects (ROI of five years).

Figure 3: ILTEC system suitable for one medium sized cooling element

7. CONCLUSION

ILTEC – the ionic liquid cooling technology – can increase safety and lifetime of metallurgical vessels and minimize production downtime. Heart of this technology is the ionic liquid ISIS B which was specially designed as a cooling medium. ISIS B overcomes all negative aspects of using water; there will be no explosions in case of a leakage as well as corrosion and hydration will not occur. Furthermore, the ionic liquid is not flammable and will not form a solid residue in case of overheating – after a shutdown the system can be restarted without the hazard of a blocked cooling element.

This technology offers a completely new way of cooling, substituting water in critical areas and cooling areas where the use of conventional cooling media is not possible. Using the ionic liquid ISIS B is a save alternative to water; furthermore this ionic liquid is recyclable and therefore environmentally friendly.

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