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Waste Water Treatment Plant for Copper Refineries

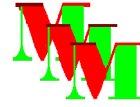
Lime Neutralization with Co-Production of Gypsum

by

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Metallurgical Viability, Inc.

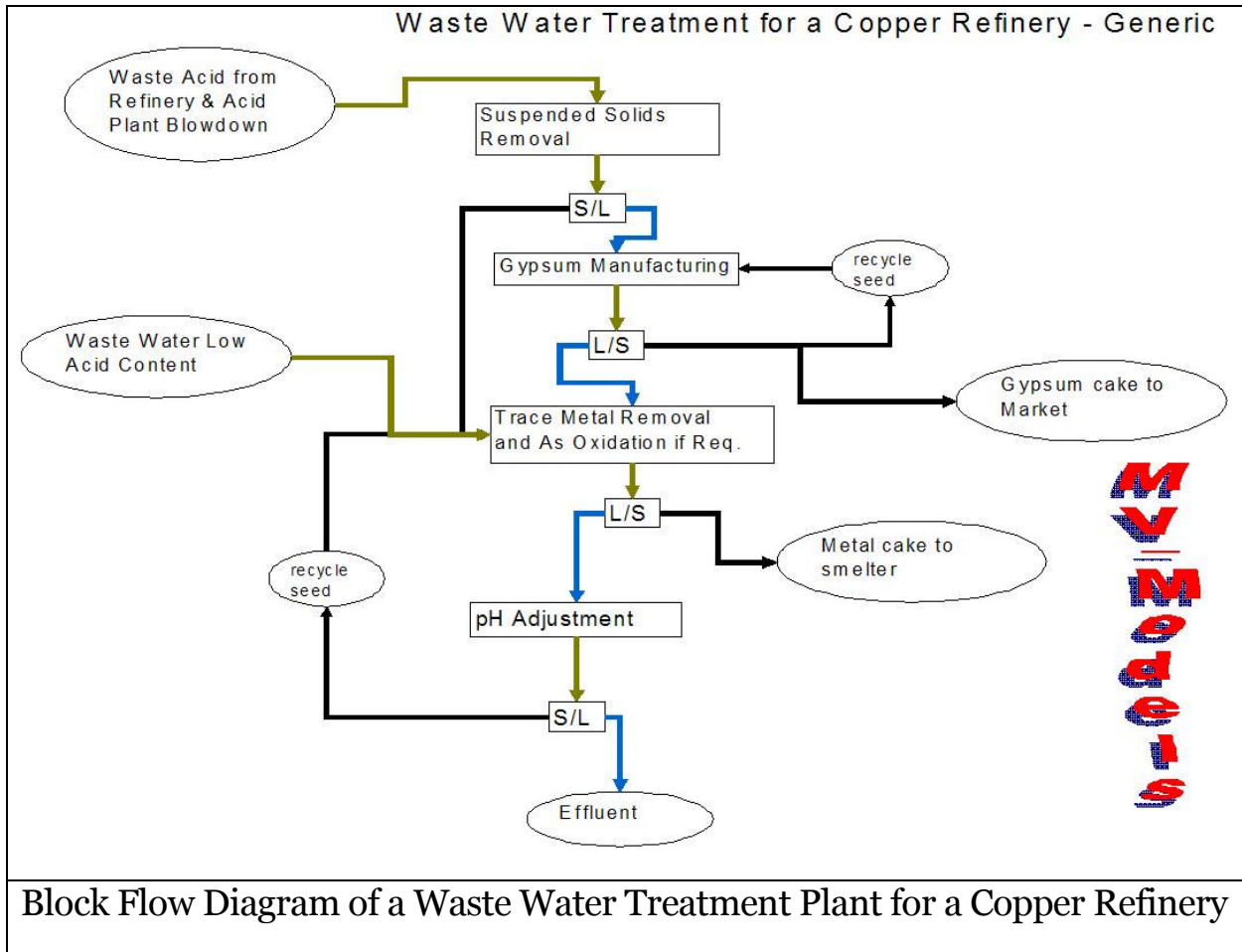
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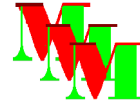


Introduction

Waste Water from a copper refinery, or any electrolytic metal/acid refinery, are unique in that they contain large concentrations of acid that must be neutralized, in general before metals are removed. In addition, they may contain large quantities of arsenic, antimony, bismuth, and other hazardous substances.

A general flow sheet is shown below:





General

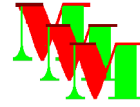
The Wastewater Treatment Plant is designed to remove heavy metals and other toxic components from the waste water. The water produced by the plant will normally be discharged into the sea, fresh water waterway, or a POWT (publicly operated water treatment). The quality of this water will meet strict environmental standards.

The Wastewater Treatment Plant will produce two products from the wastewater:

- (1) a gypsum cake suitable for use in wall board manufacturing and/or as a retarder for cement manufacturing, and
- (2) a heavy metals cake suitable for recharging into the smelter. However, this should be verified with suitable material and energy balances.

The above objectives can be accomplished by a variety of unit operations put together in many different flowsheets. However, there will be several common elements to all of these flowsheets.

The water from a smelter will not normally require treatment to meet BOD (biological oxygen demand) or COD (chemical oxygen demand). Wastewater from smelters tends to be oxidizing from the presence of sulfites and sulfates; in addition, they do not usually contain large amounts of organics, which would give rise to a large BOD. If sulfides are used in the wastewater treatment, any excess must be scavenged to avoid problems with COD.



Waste Water Streams into the Wastewater Treatment Plant

There are two categories of wastewaters into the Wastewater Treatment Plant:

- (1) those that contain large concentrations of sulfuric acid and
- (2) those that contain small concentrations of sulfuric acid, bases, and/or salts. The former is used in the production of gypsum and then fed into the heavy metals removal circuit. The later is fed directly into the heavy metals removal circuit.

Wastewater Treatment Plant Capacity

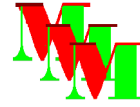
The production of wastewater from the Smelter/Refinery Complex is expected to represent most of the wastewater generated from the entire site. More than half of this water will contain high concentrations of sulfuric acid, above 200 gpl, and will be used in the production of gypsum. The other half will contain heavy metals, salts, and bases. The heavy metals to be removed including Cu, Pb, Zn, As, and other metals common to copper smelters.

Equalization Tanks

The wastewater from the various plant facilities will be collected in large, agitated storage tanks. One or more tanks will receive the very acidic waste streams from the acid plant and the copper refinery. Another tank will receive the wastewater streams from the rest of the facility including the storm water system. The purpose of these Equalization Tanks is to provide a relatively stable feed to the rest of the Wastewater Treatment Plant. It is helpful to keep a constant flow rate to the subsequent unit operations as well as a relatively constant composition. The equalization tanks should allow several days of operation with only minor changes in set points caused by changes in flow rate and compositional changes in the average waste stream being treated.

Waste Water From the Sulfuric Acid Plant

Most metal refineries using sulfide concentrates have sulfuric acid plants that convert sulfur dioxide and trioxide to sulfuric acid. Scrubbing circuits in these plants produce waste streams high in acid content and suspended solids.



The wastewater coming from the acid plant contains a high concentration of acid, both sulfurous and sulfuric acid. Concentrations about 260-gpl acids are typical. A flow rate of about 5 to 15 M³/hr is expected from a typical refinery. Since much of this acid arises from gas cleaning of the flue gases from the smelter, it also contains fumes and particulates from the smelter. The particulates are primarily the fines from the concentrate and other materials such as fluxes and recycled furnace dusts; the particulates are high in copper and iron sulfides the major components in the concentrate. The fumes come from the more volatile compounds such as arsenic, lead, zinc, cadmium, etc. Much of the fumes, usually present as oxides, dissolve in the sulfuric acid and are present in acid as metal ions. Some of the fines, present as sulfides, do not readily dissolve in the sulfuric acid, and therefore remain as suspend solids in the acid. These solids do not settle easily from the acid because of their small size and because of the relatively high specific gravity and viscosity of the acid.

Waste Water from the Refinery

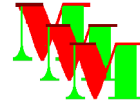
The waste stream from the refinery is a very acidic electrolyte bleed solution, containing mostly sulfuric acid and impurities that must be removed from the Refinery circuits. Concentration of sulfuric acid is expected to be about 250-gpl.. Arsenic is probably the most problematic impurity in this steam. Its removal is discussed later. Nickel also has the potential to be at substantial levels in this electrolyte; however, its removal by hydroxide precipitation is straightforward. The amount of fines in this electrolyte should be minimal.

Waste Water from the Smelter

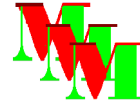
Water from the smelter comes from a variety of sources. Much of it comes from the slag granulation circuit and minor amounts come the bleed-down of cooling water circuits and from miscellaneous spills collected in sumps. The water used to cool and granulate molten slag, can dissolve small amount of metals, at the ppm level, and it can carry some suspended solids from this activity. This water should contain very little sulfuric acid and only trace amounts of heavy metals. No unusual problems are expected in treating this water.

Waste Water From Other Sources

Wastewater comes from a variety of other sources. Demineralizers and softeners produce small quantities of salt solutions that must be sent out as wastewater. Bleed downs from cooling water circuits, boiler circuits, and



some spills are directed to the wastewater plant via pumps and the appropriate piping. In addition, storm water is typically collected by a variety of drainage pipes from the entire facility into a storm-water collection pond. An initial rain after a long dry period will wash metal bearing solids into the storm-water collection pond. The storm water, containing the metal bearing solids will be sent to the Wastewater Treatment Plant for treatment. During the dry season, water is used to water down equipment and for dust control. Any excess of this water not evaporated is also sent to the storm-water collection pond. This water can also be sent to the Wastewater Treatment Plant Water.



Gypsum Production from Very Acidic Waste Water

The very acidic wastewater from the acid plant and the copper refinery must be treated separately from other waste streams. Because of the high acid stream, neutralization costs can be substantial and the quantity of salts (solids) produced is substantial. The production of a useful by-product from this acid, gypsum can offset some of the operating cost.

Reagent Requirements

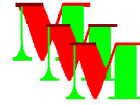
The high acid waste streams contain about 250 gpl of sulfuric acid. The primary metal impurities in this waste are arsenic, nickel, copper, and iron.

A source of calcium oxide must be furnished to produce gypsum (calcium sulfate) from the sulfuric acid. The most commonly used source is limestone (CaCO_3), although calcium hydroxide (Ca(OH)_2), referred to as lime, or slaked lime, or calcium oxide (CaO), referred to as quick lime, can also be used. (In theory, even calcium bicarbonate $\text{Ca(HCO}_3)_2$ could be used.) Limestone is typically the lost cost alternative, however, it generates carbon dioxide gas when used which can be cause frothing.

The caustic source (lime or limestone) needs to be finely divided and is typically slurried with water before use. Lime can be delivered to a site as a free flowing solid and pneumatically off-loaded to bins. It is metered from the bins to lime slurry tanks where with intense agitation it forms a solids slurry (35 % solids slurry is typical). This slurry can then be moved to a lime-slurry storage tank where moderate agitation will keep it suspended. In some localities, lime slurry can be purchased by tank truck and moved directly to storage. The least desirable is to purchase bags or bulk containers of slaked lime and manually add these to water for slurring. (Quick lime, CaO , is not recommended for this application since contact with the skin can cause burns.)

Gypsum Precipitation

Gypsum, or calcium sulfate (CaSO_4) is a salt generated by the reaction of CaO , Ca(OH)_2 , or CaCO_3 with sulfuric acid. The reaction also generates water, and when calcium carbonate is used, carbon dioxide. As with all crystallization reactions, the reaction is typically seeded with calcium sulfate recycled from subsequent solid/liquid separation steps, typically a thickener. Particle size is



controlled to some extent by the temperature of reaction and the addition rate of lime. Complete dispersion of the lime in this step is essential to get good utilization of the lime and more rapid reaction rates. This step is typically accomplished in a relatively small reaction tank to allow for proper agitation.

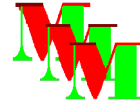
If the incoming acid has suspended solids in it, it may be necessary to remove part of these solids before adding the lime. When the calcium sulfate forms, solid surfaces, i.e., suspended solids, provide a place for the gypsum crystals to nucleate. If the suspended solids are impurities, these are incorporated into the product. Even if not incorporated into the crystals, the impurity solids will report with the gypsum cake removed from the circuit in subsequent steps.

The gypsum precipitation must be conducted at a very low pH if metal impurities are present. As lime, or limestone, is added to the system, it raises the pH. As the pH is raised, metal hydroxides are formed and precipitate with the gypsum. The exact pH that this happens depends on level of metal impurities present and their solubilities at a given pH and temperature. With the high metal impurity in this acid stream, the pH must be kept very low, perhaps, below one, to prevent the co-precipitation of metals. If the lime is not well dispersed, localized areas of low pH can form leading to metal hydroxide precipitation.

The gypsum precipitation is aided by the recycling of solids slurry for several reasons. First, it provides nucleation sites for crystal growth. As such, the size of the particles is increased by recycling. The sludge recycling also aids in the coagulation of solids in the subsequent settling and thickening step. Recycling also makes the set point of pH easier to control since some unreacted lime is recycled and the average residence time of the particles in the system is increased. Recycling a substantial portion of solids also buffers to some extent changes in composition of the incoming waste acid. The amount of recycling is restricted by the necessity of larger equipment sizes as the recycling is increased.

Gypsum Solid/Liquid Separation

Once the gypsum is formed, the gypsum solids must be allowed to settle. This is typically accomplished in a thickener. Flocculants may be added at this stage, or in the previous gypsum precipitation stage to aid in the coagulation and flocculation of the gypsum into agglomerates that settle



rapidly. These polymers can be chosen from a family of polyelectrolyte polymers, the most common being anionic or cationic polymers. The choice is made by on-site testing.

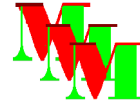
Some of the solids from the settling may be recycled to the gypsum precipitation step. Thickening may be accomplished in one or more thickeners with some solids recycling occurring counter current to the solution flow. The thickened slurry from the thickener is pumped to a de-watering step.

Gypsum De-watering

The thickened gypsum slurry must be de-watered. If properly grown, the gypsum is relatively coarse and water is readily removed. Frequently centrifuging is used to remove water from the gypsum, although filtration followed by drying can also be used. Mechanically driven centrifuges may reach adequate speeds to de-water the calcium hydroxide below 10 % moisture. Pneumatically driven centrifuges are frequently used in low moisture content is desired. (RECONTECH, a hazardous waste recycling facility, ran an operation similar to this in Illinois for several years with such centrifuges.)

If the solution retained in the gypsum contains excessive concentrations of heavy metals to meet the specification for the gypsum, it may be necessary to re-slurry the gypsum in clean water and then de-water it again.

Gypsum cake is removed from the site by truck. It is sold for use as a cement retarder or as the main component in wallboard manufacture.



Heavy Metal Production

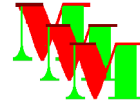
Once the gypsum is removed from the solution, the pH of the solution can be raised to precipitate the metals in solution as hydroxides. Large quantities of wet gypsum filter cake are expected from most commercial refineries. The amount will vary considerably depending on the amount of iron reagent added as discussed below.

Reagent Requirements

The most cost effect way to raise the pH and precipitate the metals from solution is again, usually lime or limestone. However, other reagents such as bases such as caustic or magnesium hydroxide can also be used. In is not in the scope of this paper to explore all of the available options. Lime is traditionally used because of its low cost, wide availability, and its compatibility to furnace operations when the heavy metals cake is recycled to the smelter. In addition, other metal precipitants can be used, for example, inorganic sulfides. Inorganic sulfides are more expensive than just neutralization, however, solubility of metal sulfides is usually several orders of magnitude lower than metal hydroxides. If compliance problems are an issue, then sulfides or more exotic precipitants, such as carbamates, need to be considered. A scavenger, such as an iron salt, can be used downstream of the sulfide addition to remove any excess sulfide in solution; this will avoid any problems with excessive COD. (If sulfides are considered, their addition rate should be controlled with a meter reading the reduction/oxidation potential of the solution.)

As discussed under the section for arsenic removal, iron salts and an oxidizer, usually, hydrogen peroxide, are frequently used to remove arsenic from solution.

Organic polymers are also commonly employed to flocculate the solids formed during neutralization. Flocculation causes particles to agglomerate into larger particles by neutralizing the charge on the particle; the agglomerated particles can be settled in a reasonable time period. Polymers can be chosen out of dozens of chemical groups of polymers the most common being cationic or anionic polymers. Specific polymers must be selected by testing on the actual waste stream. Polymers are especially effective when compliance is not being met because of the discharge of very fine, even sub-micron particles in the effluent of the plant.

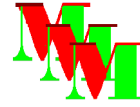


Heavy Metal Precipitation

Most heavy metals can be removed from waste by simply raising the pH of the water to about 7 to 9. The metals form metal hydroxides that are insoluble in water. Raising the pH higher than about 9 starts to re-solublize amphoteric metals like zinc, aluminum, and arsenic. In a clean system with no organics, chelators, etc. hydroxide precipitation is usually adequate to meet compliance requirements for heavy metals. However, in the presence of organic contamination, then sulfides, carbamates, or other precipitants need to be considered. In essence, organic contamination can frequently act as a metal chelator making it more difficult to precipitate the metals. The acid solution from the copper refinery is called black acid because of contamination with organics. It would be reasonable to expect some difficulty in getting to very low levels of heavy metals in the effluent when such organics are present, thus, necessitating the use of inorganic sulfides.

Another commonly used method of dealing with metals that have been complexed with organic chelators is to use iron salts to aid in the removal of other heavy metals. In this case, large amounts of iron salts, usually ferrous (or ferric) chloride or sulfate are added to the wastewater. Common practice is to add these to the solution when it is still acidic. This allows good dispersion and allows the iron to react with any chelators in the system. Added in large enough quantities, the iron will displace the other metals from their chelators making it easier to precipitate them as hydroxides or sulfides. When iron is used this way, it tends to be discharged in the effluent instead of the metal originally chelated. However, discharge standards for iron are typically 5 to 10 times higher than for other metals.

Typically, the pH is raised downstream of the iron addition. The iron will then form iron hydroxide and precipitate as a dense, heavy floc. This floc adsorbs other heavy metals on its surface and helps to lower the heavy metal concentration in the wastewater. This method will usually work at some level of iron addition; frequently, very large amounts of iron are required resulting in large volumes of sludge and the necessity for larger processing equipment downstream of the iron addition. Because of this drawback, iron is frequently replaced by more expensive metal precipitants, especially when it is being used solely to remove heavy metals. In the case of smelters, they recharge the cake to the smelter and it is generally assumed that the practice is cost effective.



Arsenic precipitation

Arsenic is present in one of two forms in wastewater streams, as an arsenite ion (AsO_2^- ; As+3) or as an arsenate ion (AsO_4^{3-} ; As +5). There are three common methods of removing arsenic from solution. All three methods work better if the arsenic is present as the arsenate ion. Therefore, if all or part of the arsenic is present as the arsenite ion, it is usually oxidized to the arsenate ion before it is precipitated from solution. The most common two methods of oxidizing the arsenic is by hydrogen peroxide, more effective at lower pH's and chlorination, more effective at the higher pH's

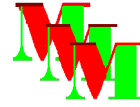
The three methods commonly used to remove the arsenate from solution include:

- (1)lime precipitation,
- (2)sulfide precipitation, and/or
- (3) iron or aluminum co-precipitation and/or
- (4) a variant of the third method,

is used if an insoluble metal precipitate is required. These four options are discussed briefly below.

Lime precipitation is an effective means of removing the arsenate ion at pH above 12. The high pH is probably only significant because it indicates that a large volume of lime has been added to the solution; hence, the method produces a large volume of filter cake. However, the cake settles well, and the filtrate is easily clarified by settling. The method has some success with arsenite ions.

Arsenate is precipitated as arsenic sulfide by the addition of a sulfide source to the solution. The most common sources of the sulfide is sodium sulfide, sodium hydrosulfide, or hydrogen sulfide. Without sophisticated reactor design, the sulfide must be added at pH's above neutral to avoid the release of hydrogen sulfide to the atmosphere. Metal sulfides, such as iron sulfide can also be used. Iron sulfide can be made insitu from sodium sulfide and iron. It has the advantage that it is much more stable than sodium sulfide sources and therefore much less likely to liberate hydrogen sulfide; it has the disadvantage that its reaction rate is much slower. Sulfides are not effective with the arsenite ion. Therefore, all of the arsenic must be converted to the arsenate ion. Excessive oxidant, however, will react to with the sulfides

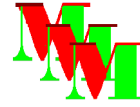


preferentially to produce sulfates. This can increase the cost of sulfide precipitation substantially. The amount of cake produced by sulfide precipitation is substantially lower than the other two methods, and the resulting filter cake has much less moisture. This method can lower arsenic in solution to the range of 10 to 50 ug/liter.

The last method, aluminum or iron coprecipitation, sometimes referred to as coagulation and precipitation, can lower arsenic concentrations to about 5 ug/liter. An iron salt is added either concurrently with a base, or upstream of the base addition. When the pH is raised, the iron salt precipitates as iron hydroxide. This precipitate is voluminous and drags down many impurities from solution. This method is most effective if the pH is kept below 9. Similarly, aluminum salts precipitate out as aluminum hydroxide at pH's above 4 or 5. The aluminum hydroxide becomes less effective as the pH is raised above 7. Both aluminum and iron produce a large volume of cake that typically filters well but retains much moisture. A variant of this method is to add the iron salt at a low pH, say pH 3 or 4, and at a high temperature, say 90C, to produce an insoluble iron arsenate given a few hours of reaction time. This method is only cost effective when disposal of the arsenic/metal cake in a landfill is under consideration.

Heavy Metal Solid/Liquid Separation

Once the metal hydroxide is formed, it must be separated from the water by some type of Solid/Liquid separation device. The most common method is to use one or more thickeners in series followed by filtration. Depending on the moisture requirements for the cake several different types of filters can be used. Rotary vacuum drum filters or belt filters are used where wet cakes can not be tolerated. High pressure filter presses, operating at 220 psig, can be used to produce a dryer cakes with as high as 80% solids.

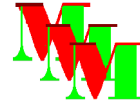


pH Control of Final Effluent

After the solids are removed from the waste water, the pH usually has to be adjusted down to near neutral before the water is discharged. This is especially true when lime is used to adjust the pH. Lime is only slightly soluble in water and therefore reacts slowly with metals in solution to make metal hydroxides. Therefore, to get reasonable reaction times, it is usually over-added and the final pH after the solids are precipitated and removed is quite high, around pH 12 is typical. Hydrochloric acid is frequently used to lower the pH to the range of 6 to 9 depending on local legal requirements.

If magnesium hydroxide or magnesium oxide (magnesia) is used instead of lime, the pH will not go above about 9. Magnesia added above this amount will simply be insoluble. As the magnesium reacts it forms soluble magnesium sulfate which leaves with the effluent. However, if sulfate restrictions exist on the effluent then magnesium treatment alone may not suffice. However, magnesia can still be used after a gypsum removal step since most of the sulfate is removed with the gypsum. Magnesium hydroxide is sometimes preferred over magnesia since the hydrolysis reaction with water to form magnesium hydroxide is relatively slow. Even magnesium hydroxide is not found common usage in smelters because of its slightly higher cost compared to lime. However, it should be considered an option if high pH solutions from using lime is resulting in deviation from effluent standards, especially if it is the amphoteric metals that are not in compliance.

When the pH is adjusted from about 12 to 7 in this step, any amphoteric metals dissolved in solution will precipitate again, usually as a very fine particulate, even sub-micron in size. These solids will leave the system as suspended solids. Very frequently, compliance problems come from the suspended solids, not the dissolved solids and are characteristic of systems where large swings in concentration occur. Usually a plant will meet its suspended solids criteria, but, the metal content of the suspended solid will cause the waste water to be out of compliance with one or more specific metals. Given the normal practices used in copper smelters, these issues should be considered.



Effluent Standards

If the smelter is located near the ocean, the effluent water, which is mixed with return seawater from heat exchangers, is returned to the ocean through diffuser piping, to minimize the thermal effects of the effluent water. A goal for the Wastewater Treatment Plant is produce water that is of suitable quality for recycling to the less demanding applications in the smelter. If these goals are met, some or all of the wastewater could be recycled for use in the smelter.

If the water is re-used, care must be taken since the water is saturated with calcium sulfate. Scaling of gypsum in pipes and other process equipment is very likely, therefore, care must be taken in using the water in critical applications; for example, this water should not be re-used in a fresh water heat-exchangers in a critical application such as cooling a furnace roof. However, it might be adequate for granulating slag or for de-dusting applications in the smelter. Mixing this water with fresh water before reuse would also reduce the probability of scaling by reducing the concentration of gypsum below its saturation level.