

TREATMENT OF SALT BATH SLUDGE AND RINSE WATER FROM CASTING CLEANING OPERATIONS

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Introduction

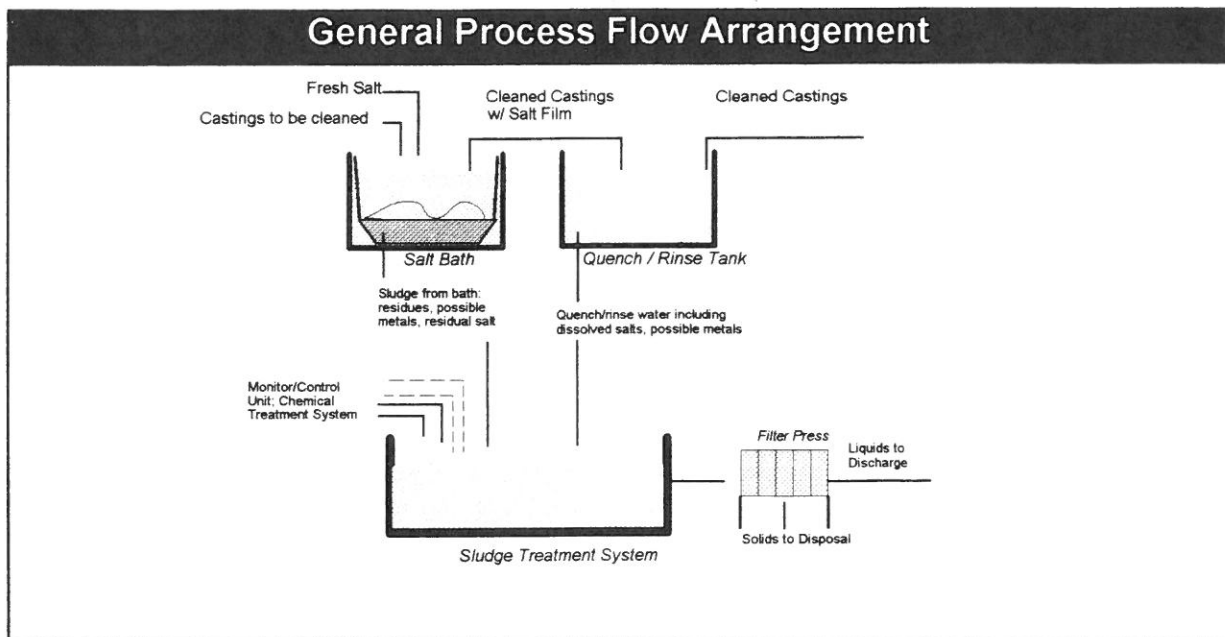
Salt bath leaching of shell and coring from investment castings is a well-established cleaning process in the industry. Its speed and thoroughness make it the fastest chemical cleaning method available. Costs associated with responsible disposal of reaction byproducts, however, have restricted its broader use and acceptance. The development of an economical and novel treatment process for reaction byproducts or "sludge" such as presented here will help to make salt bath leaching more attractive to the industry.

Background

Salt bath leaching of shell and coring from investment castings is best suited to the role of scavenger for minute amounts of residual ceramics from internal passageways and external recesses which are beyond the scope of mechanical cleaning methods. While molten salt processes are capable of removing large amounts of shell, a more economical approach is to mechanically remove any accessible shell as a preliminary cleaning step. This will minimize the amount of shell introduced into the molten salt bath, reduce the amount of process chemicals consumed, and will also minimize the amount of byproducts or sludge formed by the reaction between the shell and salt.

General Process Flow

The overall process flow is straightforward. Castings to be cleaned are immersed into the molten salt. As a result of the cleaning operation, inert ceramics along with reaction products accumulate in the bath. After some time, these materials precipitate to form sludge. The cleaned castings are coated with a thin film of salt when they are removed from the bath. A brief rinse in water quickly dissolves the salt film.



Chemistry of the Cleaning Process

Molten salt bath leaching relies on the reaction between the molten salt and free silica present in the shell and coring to be removed. The higher the free silica content of these ceramics, the more easily they are "digested" by the bath. Often, tradeoffs between cost, strength, molten metal reactivity and reactivity or cleanability in the molten salt must be made in the ceramic systems.

Refractories such as zircon and aluminosilicates present in the shell and core are generally non-reactive with molten salt cleaning processes and more or less pass through the process unchanged. They contribute to the bulk of the sludge formed during the cleaning operation, but do not consume process chemicals, *per se*. The free silica present reacts directly with the salt to form alkali silicates:



Once saturation of the bath occurs, any additional alkali silicates formed during cleaning operations precipitate out of solution and settle into the sludge collection pan. As the reactive silica is removed from the shell or coring, the physical integrity of the ceramic is degraded to the point where any non-reactive constituents simply "slough" away. The silicates, along with any inert ingredients, settle into the sludge collection pan by gravity.

The routine removal of the settled sludge, along with additions of fresh process chemical to make up for the removed sludge, maintain the bath in proper chemical balance and at consistent cleaning potential.

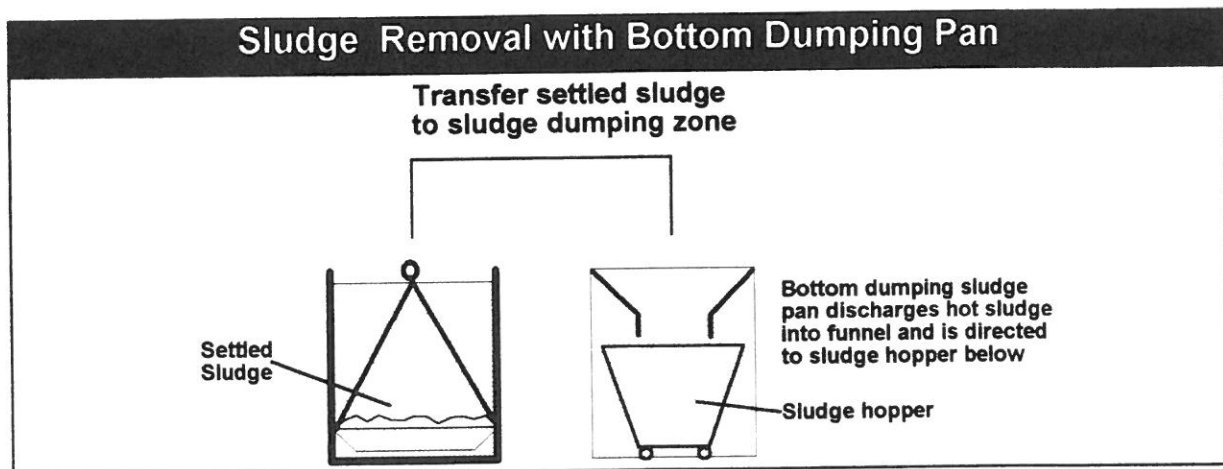
Sludge Composition

As described above, the major sludge constituents are silica reaction products and inert shell and core ingredients such as zircon and aluminosilicates. Some carbonate is also present, primarily as a reaction product of bath hydroxide with atmospheric carbon dioxide. Occluded with these materials is some good or parent salt. The precipitated sludge is somewhat porous, and is saturated with good salt; the amount of good salt removed during routine desludging can be minimized by decanting any fluid salt from the sludge collection pan before dumping. Lowering of the bath temperature to force "supersaturation" is also helpful to encourage good sludge precipitation and settling. It is not possible, however, to free the sludge completely of good salt. Some will always be present.

Sludge Removal and Dissolution

For proper long-term performance, ease of use, and operator safety, a molten salt bath cleaning system must incorporate an effective and convenient means for sludge accumulation and removal. In its simplest form, the work area is fitted with a sludge pan which simply rests in the bottom of the bath. Fitted with lifting bails, the pan is slowly removed from the working bath with the same hoist / handling system that is used to process workloads. Once removed from the bath, any liquid salt is either allowed to drain from the pan or is decanted.

Depending on the type of sludge pan used, the sludge is either dumped into a sludge hopper or an "inverted pyramid mold" via the bottom dumping opening, or allowed to solidify in the pan and subsequently removed. Once the sludge has solidified and cooled to near room temperature, it may then be dissolved in water.



A number of approaches to forming a sludge / water solution may be used. One of the more convenient methods is to place the now-cooled and solidified sludge into an empty, agitated tank. The sludge is preferably placed on an elevated grating to allow for improved water circulation to enhance dissolution. While fresh water may be used to dissolve the sludge, it is beneficial to use the quench / rinse waters from the salt bath cleaning line for this purpose. By doing so, both the sludge cake and the quench / rinse water are simultaneously treated in a single operation. Optionally, the quench / rinse waters may be treated as a separate batch.

Generally speaking, a sludge : water concentration of approximate 0.5 - 1.0 lbs sludge per gallon of water produces an easily-treatable solution. If quench / rinse waters are used as the dissolving medium, a somewhat lower sludge concentration may be beneficial in order to speed dissolving and reduce the amount of heat generated during subsequent acid neutralization of the resultant solution.

Metals Present in Sludges

In addition to the principal ingredients present in the sludge, some metallics also may be present. This is the result of metal fines, and to a lesser extent, some chemical scale conversion which may take place between the cleaning bath and foundry scales and/or oxides. This reaction occurs simultaneously with the shell and core removal, and is unavoidable. The specific metals which may be present are alloy-dependent, with chromium and nickel being the most common when stainless steel alloys are cleaned. Due to minute amounts of oxidizing agents present in the working bath, chromium compounds are most often present in the form of alkaline hexavalent chromium salts. Nickel is usually in the form of minute nickel oxide particulate.

In general, any alloying element present in the original casting being processed in the molten salt may potentially be found in the sludge formed by the cleaning process. Below is a compilation of metals contents in production salt bath sludges:

Metals in Production Salt Bath Sludges					
Metal	Lowest Found	Highest Found	Average	Allowable	EPA HW#
Arsenic	---	---	---	5.0 ppm	D004
Barium	---	12 ppm	4 ppm	100 ppm	D005
Cadmium	---	---	---	1.0 ppm	D006
Chromium	50 ppm	1500 ppm	436 ppm	5.0 ppm	D007
Copper*	3 ppm	190 ppm	35 ppm		
Lead	---	350 ppm	55 ppm	5.0 ppm	D008
Mercury	---	---	---	0.2 ppm	D009
Nickel*	6 ppm	405 ppm	108 ppm		
Selenium	---	---	---	1.0 ppm	D010
Silver	---	---	---	5.0 ppm	D011
Zinc*	2 ppm	132 ppm	23 ppm		

Notes: In the preceding table, "—" denotes "Not Detected" and should not be construed to mean "zero". Not detected means that the metal - if present - was below the detection limit of the analytical instrument used in this analysis.

Those metals with an asterisk next to them are not regulated by the Federal EPA, but are commonly regulated by state and municipal environmental agencies. For this reason, no limits or EPA hazardous waste numbers are listed for them.

The majority of these metals are insoluble at high pH levels, and in most sludge : water solutions would separate without further treatment. The notable exception is chromium when present in its hexavalent (Cr^{+6}) state. This particular form of chromium is soluble in water over the entire pH spectrum, from strongly acidic to strongly basic. It is necessary to chemically reduce the chromium to its trivalent (Cr^{+3}) or divalent (Cr^{+2}) state and then subsequently precipitate it as chromium (III) hydroxide or chromium (II) hydroxide.

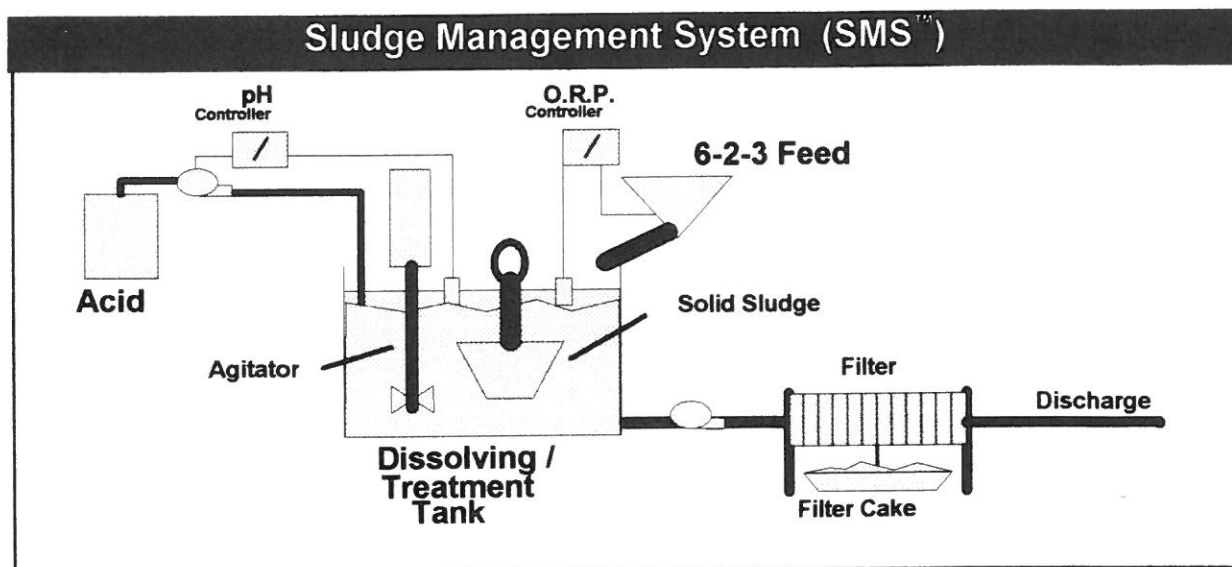
Conventional Chromium Reduction / Precipitation

Conventional chromium reduction requires a bidirectional adjustment of pH to accomplish chromium reduction and precipitation. The commonly-used reducing agents such as sodium metabisulfite require a relatively low pH value (usually pH = 3 or lower) to be effective. Once the chromium has been reduced at these low pH values, it is still soluble. The pH must then be increased by adding alkali until the final pH is sufficiently high to form the chromium hydroxide precipitate:

- [1] Add acid to lower pH of solution
- [2] Treat with reducing agent
- [3] Add alkali to raise pH of solution

Chromium Reduction with Kolene® 6-2-3 Reducing Agent™

This treatment method utilizes a reducing agent which is effective in reducing the hexavalent chromium at high pH levels. The amount of reducing agent required can be calculated based on the chromium content of the solution, or may be automated by the use of an Oxidation - Reduction Potential (ORP) probe along with appropriate control and feed devices. The pH of the treated solution is then adjusted with acid additions to the range of approximately 8.0 to 8.5. As the pH of the solution is lowered, the reduced chromium species form insoluble hydroxides and precipitate.



After chromium reduction and pH adjustment, the solids must be removed from the solution before it may be discharged. This may be accomplished in a number of ways, ranging from simple gravity settling to filtration, with a filter press being a common method. While the restricted metals have been removed from the water solution, they will be present in the solids filtered from the solution.

To determine ultimate disposal classification for the solids, they must be subjected to Toxic Characteristic Leaching Procedure (TCLP) testing. This test simulates what may happen to a drum or other container of waste if it should corrode, rupture, or in some other way no longer effectively contain the waste and subsequently come into contact with ground water. (This is the same test procedure which raw, untreated sludges are subject to prior to disposal.) The main objectives of the test procedure include corrosivity and restricted metals content of the waste.

The leaching solution used in the test is a limited amount of moderately-weak acid. In many instances, the leaching solution is sufficiently strong to solubilize metals which may be present in the waste. This would result in the waste being classified as a hazardous material, and dictate a more costly, scarcer disposal site.

An unique characteristic of the 6-2-3 Reducing Agent is its ability to micro-encapsulate and/or immobilize metals present in the filtered solids. In many cases, this treatment renders the metals non-leachable when a representative sample is subjected to the TCLP procedure. The result is a treated sludge which is not corrosive, and does not present a disposal hazard as evidenced by "passing" TCLP testing.

Below is an example of sludge before and after treatment with 6-2-3 Reducing Agent and subsequent neutralization with sulfuric acid:

Sludge Before & After Treatment				
Parameter	Before ¹	After ²	Allowable ³	EPA HW# ³
pH	13+	9.53	< or = 12.5	D002
Arsenic	4---	---	5.0 ppm	D004
Barium	3 ppm	0.16 ppm	100 ppm	D005
Cadmium	---	---	1.0 ppm	D006
Chromium	650 ppm	0.13 ppm	5.0 ppm	D007
Copper*	16 ppm	---		
Lead	17 ppm	---	5.0 ppm	D008
Mercury	---	---	0.2 ppm	D009
Nickel*	6 ppm	---		
Selenium	---	---	1.0 ppm	D010
Silver	---	---	5.0 ppm	D011
Zinc*	4 ppm	0.48 ppm		

Notes:

- ¹ The "before treatment" sample was completely dissolved utilizing strong mineral acids. The metals reported for this sample would therefore be a "worst case", as all metals present would be in solution.
- ² The "after treatment" sample was the filtered solids after complete sludge treatment, and was analyzed using the prescribed TCLP protocol.
- ³ Those metals with an asterisk are not regulated by the Federal EPA, but are commonly regulated by state and municipal environmental agencies. For this reason, no limits or EPA hazardous waste numbers are listed for them.
- ⁴ "---" denotes "Not Detected" and should not be construed to mean "zero". Not detected means that the metal - if present - was below the detection limit of the analytical instrument used in this analysis.

Economics of Sludge & Rinse Water Treatment

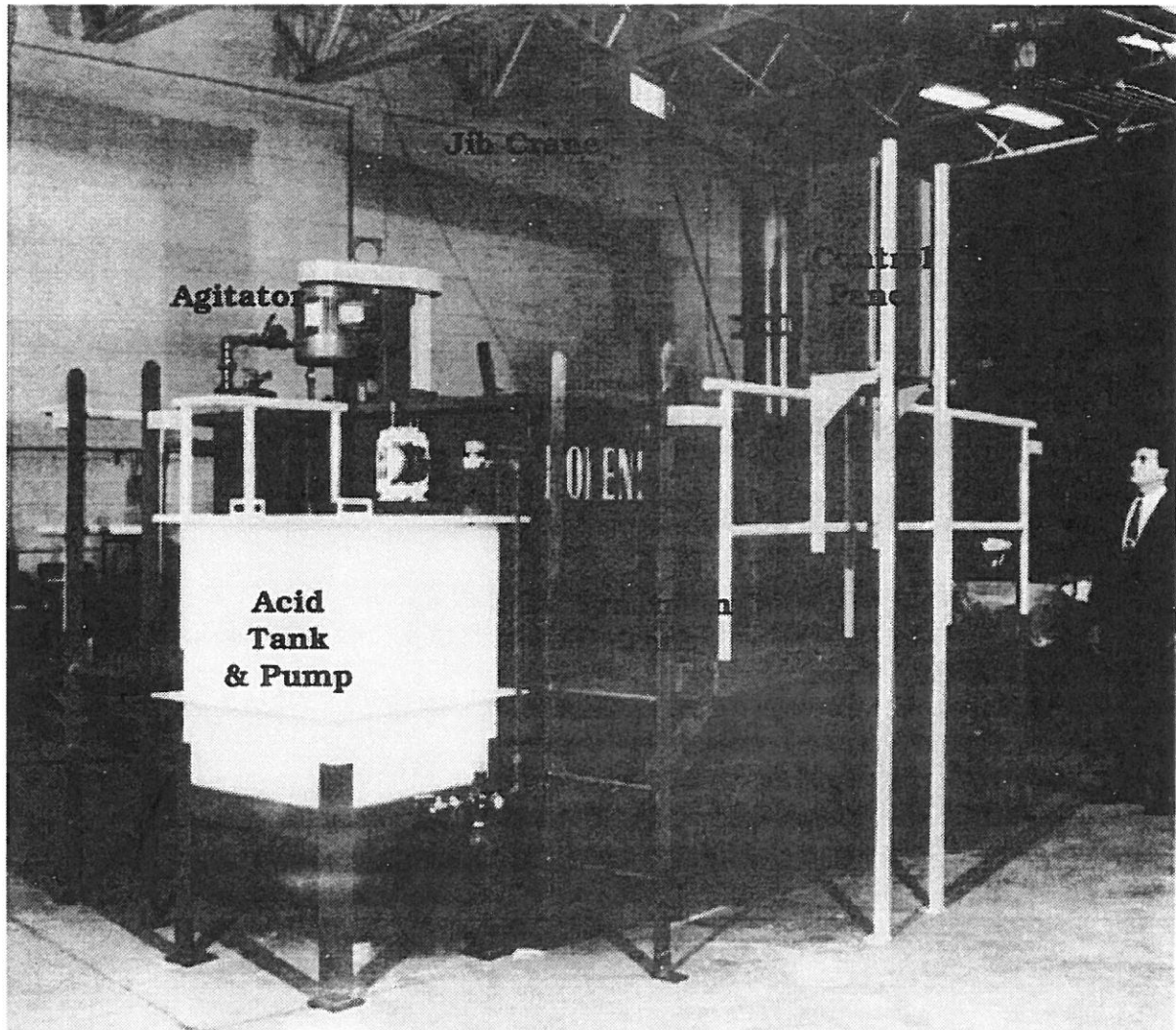
To be commercially viable, in-house treatment of sludges and rinse waters must be economically attractive. The following broad guidelines are helpful in determining the approximate costs involved to treat sludge:

Comparison of Treatment vs Disposal of Sludge	
Conventional sludge disposal, hazardous waste site, per 800 pound drum	\$ 300.00
Sulfuric acid to neutralize 800 lbs sludge, at 1 lb/lb sludge	81.60
6-2-3 Reducing Agent™ to treat 800 lbs sludge, @ 100 ppm Cr ⁺⁶	9.60
Disposal costs for non-hazardous filter cake, 800 pound drum	30.00
Total costs for treatment & disposal of sludge	121.20
Savings realized by treating vs disposing of sludge:	\$ 178.80

Based on these approximate costs for conventional disposal, chemicals required for in-plant treatment, and disposal of the treated filter cake, the savings associated with sludge treatment versus conventional disposal can be calculated. In addition to this figure, labor rates and investment for the required sludge treatment equipment would have to be factored also.

Summary

Based on both laboratory-scale testing and field installations, the in-house treatment of salt bath rinse waters and sludges from casting cleaning operations is feasible and cost-effective. The general treatment process is straightforward, and may be automated to reduce required manpower and to increase reliability of the treatment process.



Example of Sludge Management System (SMS™)