METALS AND ALLOYS WATER SOLIDIFICATION A BRIDGE FROM PYRO- TO HYDRO-METALLURGY

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Abstract

The increased tendency to use hydrometallurgy as an extraction step towards final refining following a pyrometallurgical smelting process requires melts which have to be cast and or comminuted which can then be taken up into solution or leached.

To generate surface area for optimal leaching, a common process is to granulate and in many cases mill, which is a general practice with friable material with properties associated with higher sulphur, carbon and silicon levels. However, in the case of metallic melts milling can be unfeasible due to the ductility of the granulated particles.

Water solidification is capable of producing either fine particles by means of granulation or atomisation. Atomisation however, can produce particles as fine as 40 microns without a milling circuit.

Introduction

In comparison where over the last century where once a colourful mineral was smelted and then perhaps the resulting raw metal electrolytically refined, there is now a huge range of process routes to cope with ever leaner and more complex metal resources, both primary and secondary. Progress has now allowed for waste materials such as tailings and slags to become new resources.

Many new technologies have been developed in hydrometallurgy, with such methods as solvent extraction and high pressure hydrogen reduction being added to classical precipitation and chemical methods. Hydrometallurgy has been used for centuries in precious metal refining, but is now widely used for metals such as Co, Cu, Ni, Ta, Nb etc. In many cases, the flow sheet can be very schematically represented as in Figure 1.

In hydrometallurgy, the first stage is to take the metal up into solution, sometimes completely, or sometimes selectively (leaching to leave behind another metal). In either case, a large surface area is needed to speed up the reaction. Also to enable attack to proceed rapidly, a fine powder is needed so that it may be easily suspended in the reagent liquid without excessive stirrer power. Typically maximum powder sizes of the order of 250microns (60#) and median sizes of 40-75 microns (400 – 200#) are preferred.

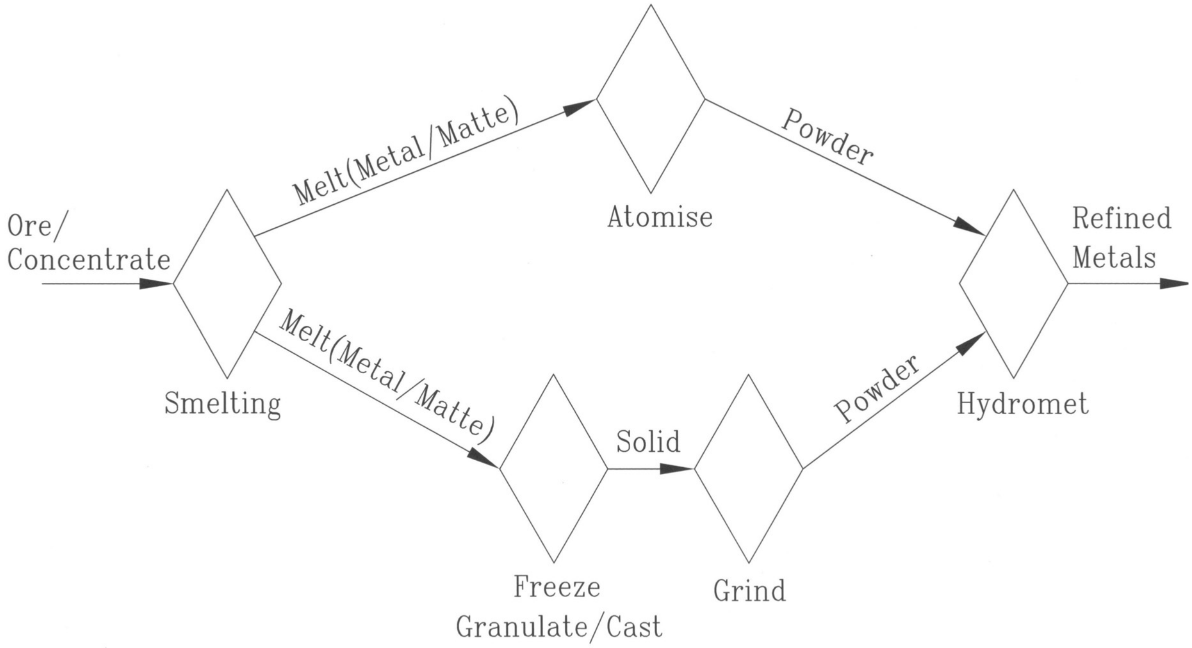

Figure 1: Schematic flow sheet of combined pyro- and hydro- metallurgical processing.

To make such powder of a brittle material like ore is very simple. Crushing and grinding as part of ore beneficiation are carried out on a colossal scale in the mining and mineral industries. However, metals are ductile and thus other means must be applied to achieve size reduction. Developed for the production of metal powders for high value uses, atomisation is now dominant in this field. Atomisation is the break-up of a stream of liquid into a spray. In the case of a molten material, the spray naturally cools very rapidly and solidifies into a powder. Clearly it is much easier to disrupt a liquid than a solid, and as the metal powder industry has grown, increased scale and better technology have lead to a state of the art where applications to intermediates in smelting are both technically and economically feasible.

Granulation can be classified as a low-pressure (2-6bar) water atomisation process where particles ranging from a millimetre, and with certain alloys, up to a centimetre in size can be produced. “Atomisation” is in effect a high pressure (20-200bar) granulation process to make powders finer than a millimetre, ranging as small as 10 microns in some cases. A key advantage of atomisation over mechanical size reduction is that particle composition is extremely flexible; generally if an alloy can be melted, it can be atomised to a powder of the same composition. Mechanical properties of the solid are irrelevant. However those of the liquid are important, and the very low viscosity and surface tension of high sulphur mattes means that they are particularly easy to break up into fine droplets. This means that atomisation pressures can be markedly reduced and thus capital and energy costs.

History of atomisation

While the history of atomisation is not reliably reported, it is clear that the basic concept was known to Agricola in the 16th century who describes granulation of molten metal. In Victorian times, it is likely that atomisation of tin and solder was introduced to make pastes for plumbing and by 1915 Prof Hall in the USA patented atomisation nozzles for aluminium, used in explosives. This early work involved using compressed air, or the readily available steam, as an atomisation medium, and air is still quite widely used for processing aluminium, zinc and copper alloys at rates typically in the range of 0.5-3t/hr.

During the 1930s and 40s work was done on using air and water jets to process copper alloys and cast iron, and much pioneering work on the processing of alloys of Fe, Ni and Co was done by Dr Jones in England in the late 40s and early 50s. This lead to commercial applications such as stainless steel filters, and shortly afterwards, the large scale (10-30t batch) water atomisation of carbon steel powders, which are now produced in plants with capacities up to 50t/hour with world output approaching 1Mt/yr and several plants claiming capacities of over 200kt/yr.

It is this technology for routine large-scale and low cost processing of melts that is now available to the metals industry and is now becoming accepted as a viable alternative to older methods.

Applications in secondary metal processing

Naturally, the first applications of atomisation were where the drivers were strongest and the technical difficulties least. The strongest drivers are in the refining of precious metal scrap which needs particularly aggressive chemicals to dissolve. The ductility of such metals makes mechanical comminution totally unfeasible.

Silver-copper scrap/bullion

The processing of silver-bearing scrap or bullion with Ag levels from 20-90% has been done for many years by melting the material and granulating it. The resulting granules were leached by acid to remove copper etc and leave a silver rich sponge behind for subsequent remelting and electrolytic refining. However it was found that leaching times were long (8 hours or more) and there were always problems due to the heavy section of the granules. If over-leaching was done, significant amounts of silver could be dissolved, whereas under-leaching would lead to excessive copper in the sponge. Developments in the industry led to a water atomiser to process 300kg melts of alloy into fine powder which could be leached in under an hour under much better control.

Platinum-Rhodium scrap

Platinum is exceptionally difficult to take up into solution, and extremely aggressive acid mixtures are needed. As Rh levels rise in PtRh alloys, they become more and more stable until Pt30Rh is almost impossible to attack. Some refineries even resort to using pure platinum as a diluent to make a lower Rh level melt that is granulated and then dissolved. This is extremely costly. A far more elegant solution is to melt the bulk scrap alloy and atomise to a fine powder. This can be taken up into solution much more controllably (and with less pollution problems) than the bulk, and even Pt30Rh alloy is thus rendered soluble.

Alternatives for primary smelting

In the extraction of metals from primary sources, the smelting of concentrates to mattes or metallic melts with various levels of sulphur is a very important process for many metals. The alternatives currently utilized and the attractions of atomisation are set out below.

Granulation/casting and Milling

The sulphide smelting industry is familiar with granulation, as practised for Cu, Ni, Co and Pt slags or mattes and also with milling of the mattes to obtain particles in the 10-200 microns range for further processing. Such fine materials are increasingly needed for hydrometallurgical processing by a range of leaching or solution methods, or for pyrometallurgical processing in flash smelters.

The traditional method of producing a fine powder is to granulate and then mill the matte or to cast in sand pans or casting moulds, and then on to crushing and milling. This route is possible if the material is brittle (friable), which is a property associated with high sulphur level mattes. For lower sulphur levels, where the matte is less amenable to milling, the cost of the milling increases with regard to capital costs, energy costs and maintenance costs due to severe wear problems. At sulphur levels below a few percent, milling becomes very unattractive.

Atomisation in Sulphide Smelting

Atomisation allows the conversion of the liquid matte to powder in one fairly straightforward operation. Apart from the advantage of having one less step in the process compared to granulation and milling and four less compared to casting, crushing and milling, there is also the advantage of dispensing with all attrition components in the milling process.

It is therefore attractive to consider atomisation to replace milling and grinding in extracting Cu, Ni, & Co from sulphide ores, and to use similar process routes in extracting the metals from Cu, Ni, Co, – bearing dumps where slag is reprocessed via the smelting route. The alloys produced from this reprocessing are low in sulphur and hence ductile, and not suited to processing by crushing and/or milling.

Clearly, while atomisation with high-pressure water is generically related to water granulation, the much higher water pressures (20-200bar compared with 2-6bar for granulation) affect the equipment design significantly. It is relatively expensive to pump all the water needed to extract the heat from the melt without it boiling (typically 5 or 6 times the weight of metal is needed). Using special designs, a high-pressure water flow of only 2-3 times the melt flow can be used to break up the melt, with additional low-pressure water added for cooling.

Safety Aspects

Granulation is normally carried out by running the melt down a launder and melt flow rates can vary drastically. This is a major factor contributing to the risk of water/metal explosions, ranging from the audible to the destructive/catastrophic. In order to achieve a consistent fine particle size in atomisation, the water jets are relatively small in dimensions and the flow of metal must be much more consistent. Thus a tundish is used (similar to those in early continuous casting machines), typically having a capacity of 1-3 minutes flow of metal. The tundish is fitted with a metering nozzle to maintain a reasonably consistent (say +/-20%) flow rate of melt into the jets. Water/metal explosions are extremely rare in such systems. The other hazard that can arise, that of hydrogen generation due to partial reaction of the melt with the water, is readily controlled by forced ventilation, or, in some cases, inert gas purging.

Energy Input Comparison

With any process that involves increasing surface area there is a requirement for energy input. This energy is derived from the water in atomisation or from the impact of the ‘balls’ in the ball mill. Ball mill productivity is strongly product dependant, but typical figures for energy consumption lie in the range of 3-30kWhr/t depending on the alloy milled. The power requirement for high-pressure water is much greater than with a granulator - to make 30-40 µm median CuNiS matte powder at 1tonne/minute, the energy required for the H.P. pumps is around 550kW. This compares with 210kW for granulation. However when we calculate the energy per tonne, the atomiser works out at 8-10kWh/t, while the granulator is around 3-4kWh/t to which we must add the milling energy of 3-30kWhr/t to give a total of 6-34kWh/t.

Thus, in comparison with granulation and milling, atomization involve little, if any increase in energy consumption, and in the case of tougher materials may effect major savings, perhaps up to 70% or more.

Process Comparisons for a 60ton/hour plant output

We can consider three alternative process routes for a sulphide ore smelter and compare the energy consumption in kWh/ton and initial capital cost of each process. Capital costs are not absolute, but are all estimated on the same cost structure to give good comparative figures.

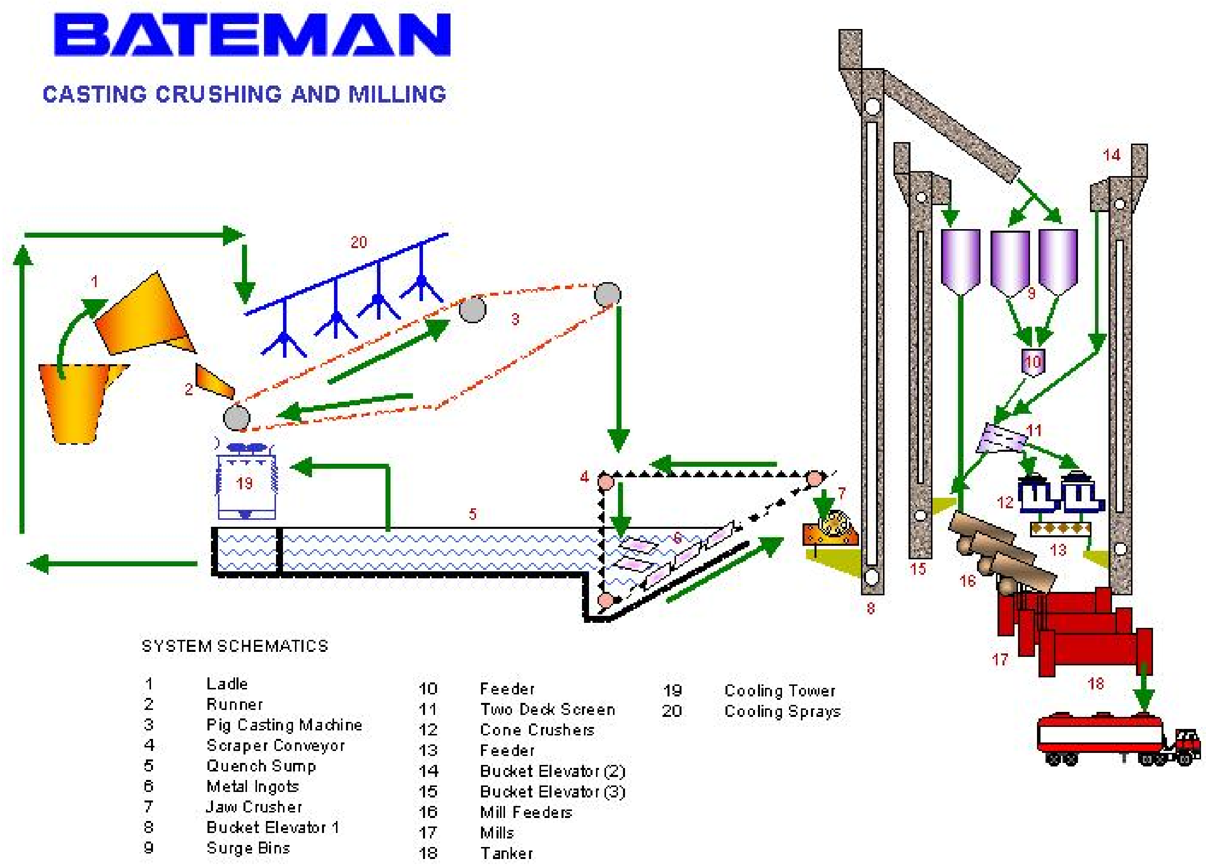

Figure 3: Casting, crushing and milling process flowsheet

<u>Casting, Crushing and Milling</u>

An air-cooled dry process (Fig 3) consisting of Casting, Crushing and Milling will require a Pigcaster, Scraper conveyor, Cooling circuit to cool pigs for feedstock to the primary Jaw Crusher on to the Two stage Cone Crushers and finally the Mill via suitable feeders and screens. This process then requires the powder to be slurried for pumping to hydromet and then resultant return water storage must be provided.

This process will require 27,0kWh/ton. However it entails 6 individual process steps with the resultant handling from one to the other making it maintenance and operationally intensive. Each of these processes plus interface handling equipment will be subject to high wear and therefore high maintenance cost with frequent repair and even replacements. Capital input for the initial plant will be in the region of US$ 10 million.

Granulation and Milling

Granulation and milling (Fig 4) will require a Granulator, de-watering, milling and re-slurrying for pumping to hydromet. This process will require 26,6kWh/ton. However it entails 4 individual process steps with the resultant handling from one to the other again make it subject to a lot of wear and thus maintenance. although only the granulation de-watering and milling is purely mechanical however de-watering could also be achieved statically by way of novel design. Capital input for the initial plant will be in the region of US$ 7 million

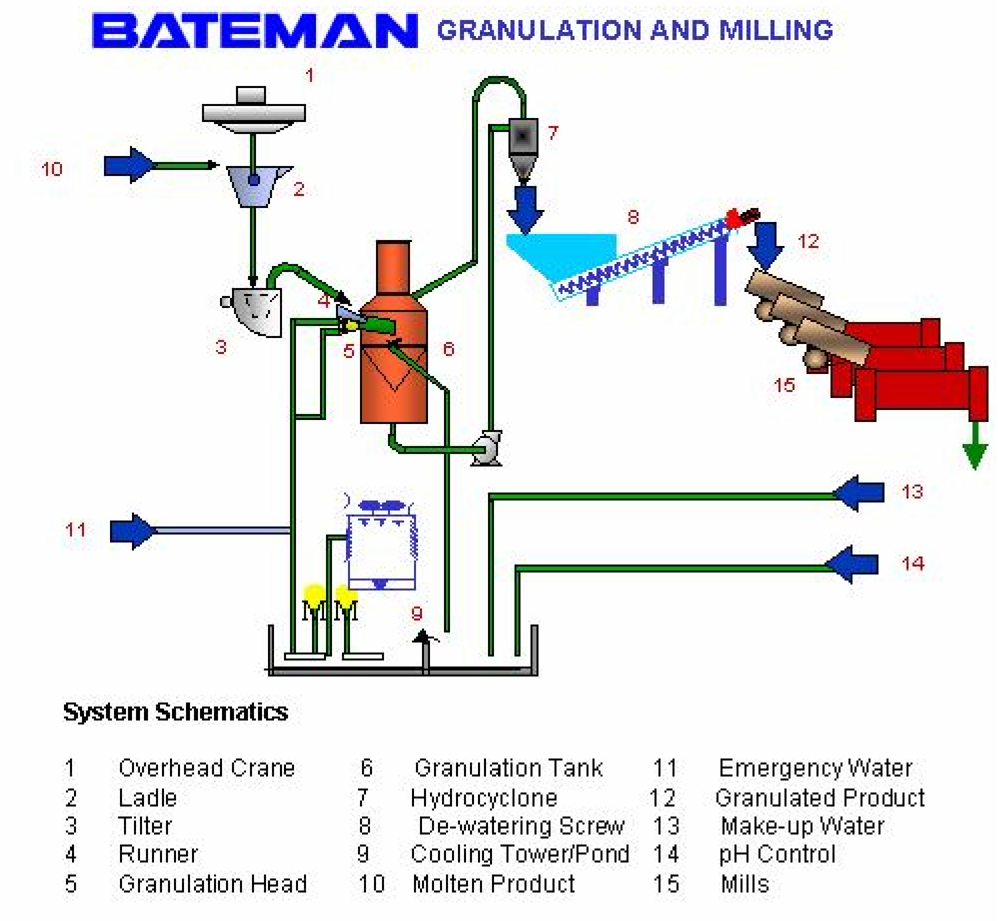

Figure 4: Granulation and milling process flowsheet

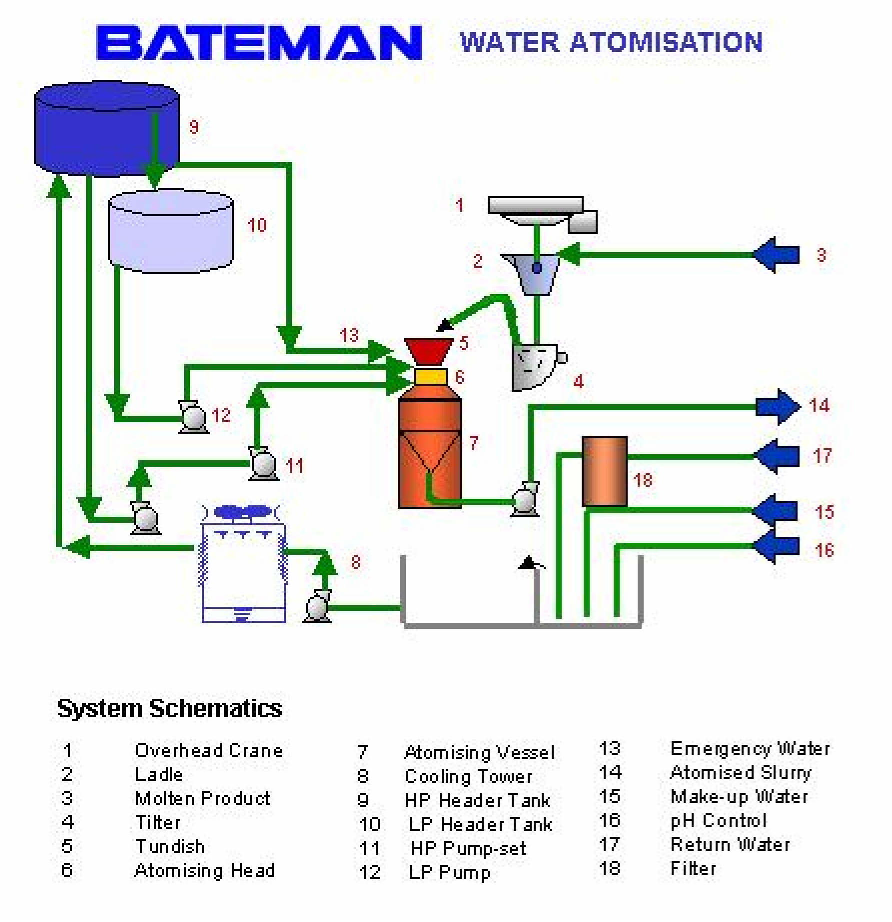

Figure 5: Atomisation flow sheet

Atomisation

Atomisation (fig 5) on other hand is a one step process that will require 28,6kWh/ton, fractionally more than other processes however there is no mechanical equipment involved apart from the pumps which are also required in the other processes although at a much lower pressures. Capital input for the initial plant will be in the region of US$ 5 million

Future developments

The concept of using atomisation in large scale smelting is as yet a novel one and there are many new possibilities opening up. For instance it could be used to process matte prior to pressure leaching in CuNi ore smelting. It could also be used to process copper matte from a first stage smelting to a powder suitable for flash converting. While the first applications have come in the processing of fully metallic melts which are fairly ductile and hard or impossible to mill or crush, the economic attractions of atomisation will probably see it adopted in future even for brittle high sulphur materials. These are actually easier to process than low sulphur metals due to low surface tension and viscosity, resulting in cost savings. Compared to milling where multiple units are often needed, atomisation is a highly productive process allowing a single stream unit to produce powder at 60t/hour and multi-stream units (fed by multi-orifice tundishes like multi-strand casters) to produce at large multiples of this, up to 100s of tonnes/hour. The capital cost per installed unit of output of such units will fall rapidly with size. In addition to the attractions of their capital and energy costs, atomisers use water sprays to break up the melt, and water sprays do not wear out. Compared to mechanical comminution equipment the maintenance costs of atomisers should be considerably reduced.

For process engineers considering the flow sheets of new projects the ability of atomisation to “collapse the process flow sheet” by eliminating multi-stage operations in favour of a more direct route will be considerable. The physical size of atomisers in modest; a typical large unit might be a vertical vessel 3m tall and 2m diameter, so the amount of expensive building and cranage can be reduced. Material handling is simplified by the atomiser directly making a slurry that can be pumped easily out of the hot bay to a separate hydromet building.