TRAVAUX 48, Proceedings of the 37th International ICSOBA Conference and
XXV Conference «Aluminium of Siberia», Krasnoyarsk, Russia, 16 – 20 September, 2019

Techno-Commercial Evaluation of Chloride Based Production Routes for Technology Metals and Materials

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Abstract

Chloride-based hydrometallurgy has historically been constrained to small and medium- scale niche-applications, as it puts high demands on the installed equipment, surrounding buildings and infrastructure in terms of corrosion resistance. Besides that, HCl and Cl_2 are not always available as cheap captive by-products from other chemical processes, and the handling of chlorine containing processing wastes poses various challenges. However, in certain industries, such as Aluminum and Nickel, as a consequence of either depletion of their traditional raw materials base, the demand for extremely low cash cost or for geostrategic reasons, producers are becoming increasingly open to consider novel flow sheets, based on leaching non-conventional primary or secondary feedstocks in hydrochloric acid before applying various separation and extraction steps.In the present paper, we will briefly introduce the building blocks of a Chloride-based flow sheet for a metallurgical process. We will then introduce a hypothetical flow sheet for a processing plant for the production of Smelter Grade Alumina (SGA) from Aluminous Clay (Kaolin), identify the technical challenges and economic success factors involved, present as well as compare several technical options and summarize our findings and recommendations.

Keywords: Chloride, Hydrometallurgy, Alumina, Economic Evaluation

1. Introduction

Despite metal chloride systems lending themselves to a variety of well-established and efficient metal separation techniques, such as selective volatilization and distillation, selective crystallization, oxidative precipitation, electrolysis, hydrolytic distillation and pyrohydrolysis, their use in industry remains fairly constrained to niche domains, such as the descaling of hot rolled steel in hydrochloric acid baths with closed-circuit regeneration of HCl by pyrohydrolysis, the production of titanium dioxide pigments or sponge titanium from (synthetic) rutile or chloride slag by means of fluidized bed chlorination (with carbonaceous reductants added) and production of synthetic carnallite or anhydrous $MgCl_2$ by similar processes with subsequent electrolysis of Mg metal.

The volatile and corrosive nature of hydrochloric acid, that frequently leads to a quick detrition of the surrounding buildings, requires the constant attention of experienced operating and maintenance staff, while Cl_2 leaks (or emergency blow-offs) pose a substantial health hazard.

Although reasonably sophisticated technologies for the recovery of Cl_2 and HCl from certain metal chloride solutions have been developed, only trivial cases, involving relatively pure or favorably composed solutions, yield attractive recovery rates beyond 98% in industrial setups.

This, in combination with the extreme requirements for corrosion and abrasion resistance put on the installed processing equipment (valves, pumps) by hot brines and slurries, as well as the sticky, scale-forming nature of certain chloride based liquid/solid mixtures as described in [1], has historically limited the application domain of chloride hydrometallurgy to cases, that are either technically straight-forward (pickling of carbon steel, where iron is the predominant metal and the effects of the most common alloys/impurities on process performance are benign) or economically very attractive (pigment or Ti metal production, where chloride technology applied to traditional feedstocks yields lower cash cost, a reduced environmental impact and in many cases a superior product than the competing sulfate technology.

The prime motivators to – despite its challenging characteristics from an engineering perspective – still consider flow sheets based on chloride hydrometallurgy may differ from industry to industry.

Some industries (such as Nickel [3] where laterites in the long term will replace sulfates as the prime source) may face circumstances under which conventional feedstocks, which lend themselves to reasonably economic processing , are becoming scarce and have to be replaced by sources, that are more readily processable by chloride, than sulfate or smelter technology. Others may have difficulties getting expansions of their tailings dams (e.g. Bauxite Residue disposal areas at alumina refineries implementing the Bayer process) permitted and thus require processes with a minimized (in at least the dimension constrained by the permit) ecological footprint. Certain smelters may be under regulatory pressure to reduce their emissions or to re-utilize their slag instead of disposing it. Yet another corner of the industrial landscape may be motivated by changing their resource base from imported to domestically available materials to mitigate geostrategic risk or the burden of comparatively high transportation cost as a consequence of the relative remoteness of processing capacity.

Finally, some companies may eye winning their products by means of recycling out of waste (e.g. urban mining) instead of relying on conflicted primary sources potentially linked to slavery and child labor (as e.g. for at least some of world's Cobalt and Tantalum), where again they may benefit from the versatility and potentially high selectivity of a chloride based flowsheet.

2. Basic Operations in Chloride Hydrometallurgy

2.1. HCl Leach

As described in [2] most flow sheets based on chloride hydrometallurgy naturally "start" with dissolving some feed material in hydrochloric acid and/or another reactive chloride species (potentially improving reaction kinetics). This feed material may for example be an ore, a concentrate, a slag or other waste material, but also an ultra-pure source of a metal from which an oxide of particular chemical and physical properties is to be produced.

For many ores (such as in the focus of this paper: Kaolin), concentrates or slags, some thermal pre-treatment, pre-reduction or pre-oxidation may significantly improve their amenability towards leaching at moderate temperatures and pressures.

2.1. Oxidation and Oxidative Precipitation

Oxidation of some metal chloride solutions yields chlorides of a higher oxidation number as well as metal oxides, which can be precipitated or – for combinations of certain species, such as iron and vanadium – co-precipitated.

2.3. Selective Crystallization

Metal chlorides have sufficiently different water-solubilities and can thus be selectively precipitated by oversaturating the containing solution with (e.g.) HCl.

by placing such a plant in a location with favorable labor and construction cost or particularly well suited existing infrastructure.

On another note, the presented economic analysis is based on an SGA price of 320 USD/t. Higher prices will yield higher expected IRRs.

It may obviously also be very worthwhile exploring (leveraging substantial synergies) to upgrade at least a part of the alumina production to HPA and sell it into the fast-growing market for high purity alumina (at the date of writing selling at 30.000 USD/t) at healthy margins, which could well support the case for the basic SGA business.

Finally, the technical challenges posed by the – unprecedentedly for a HCl leach based operation – large scale of an installation of an industrially meaningful capacity are not to be underestimated.

The required scale-up from known laboratory test plants and/or similar plants for the production of high purity alumina shouldn't be undertaken without one or two intermediate steps of piloting and optimizing the underlying concept at different intermediate sizes while at the same time getting more certainty on the true expected capital and operating cost structure.

5. References

1. Herbert Weissenbaeck at al., Development of Chloride Based Metal Extraction Techniques – Advancements and Setbacks, *Proceedings of the ALTA Nickel-Cobalt-Copper Conference 2013*, Perth, Australia, 25 May - 1 June 2013
2. Dieter Vogl at al., Development of a versatile HCL-leach based metal extraction technology stack, *Proceedings of the ALTA Nickel-Cobalt-Copper Conference 2012*, Perth, Australia, 26 May - 2 June 2012
3. Benedikt Nowak at al., Nickel extraction from laterite ores by leaching with hydrochloric acid, *Proceedings of the ALTA Nickel-Cobalt-Copper Conference 2012*, Perth, Australia, 26 May - 2 June 2012
4. Douglas W. Hubbard, How to measure anything, *ISBN-13: 978-1118539279*
5. Wolfgang Steinbach, Hydrochloric acid recovery in metallurgical applications through pyrohydrolysis, *PhD Thesis, Vienna University of Technology, 2002.*