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Recovery of acid and oxide by-products from spent pickling liquor

The recovery of hydrochloric acid from spent pickling liquor by pyrohydrolysis is not only environmentally advantageous in that it removes the need to neutralise and dispose of spent acid and that it reduces water consumption. It is also highly cost-effective, as it eliminates disposal costs, reduces the cost of replacement acid and generates a valuable oxide by-product.

Figure 1. Powdered oxide from the spray roast process (left) and granular oxide from the fluidised bed process

Because of numerous technical advantages, hydrochloric acid has, in recent years, come to dominate the market in pickling agents and also as a solvent for ore dressing. Yet the enormous input required to procure fresh acid and dispose of or neutralise spent acid constitutes a major economic factor in operating pickling plants and ore treatment plants.

Acid regeneration plants eliminate the need for and cost of disposal of spent acid and the cost of replacement hydrochloric pickle liquors, making the plant virtually self-reliant. At the same time they reduce emissions and thereby the impact of the plant on the environment.

For acid regeneration, the spray roaster and fluidised bed technologies were developed. The processes regenerate spent hydrochloric acid from continuous and push-pull pickling lines at recovery rates of up to 99.9%.

Regeneration by pyrohydrolysis

Hydrochloric acid regeneration using pyrohydrolysis provides total recovery of a spent acid solution into a metal-free product. Operators not only recover hydrochloric acid in its free and bonded state, but also obtain high-quality iron oxide, either as pellets or fine powder, which is in strong demand by the ferrite, pigment and other industries.

Pyrohydrolysis is the chemical conversion of metal salts using steam and oxygen at high temperatures. Depending on the temperature of pyrohydrolysis the oxide product is either in granules if treated in a fluidised bed plant, or as a powder, if treated at a lower temperature in a spray roast plant. The spray roast process works at a temperature well below the sintering temperature of iron oxide so that this will be obtained as a red powder, typically less than 1 µm in size **(figure 1)**.

On the contrary, waste acid roasted in a fluidised bed operates at a higher temperature which sinters the oxide forming granules in the size range of 0.2 mm up to 2 mm. The sintered iron oxide granules are free of dust and do not contain residual chloride. The products are easy to store and can either be recycled for steel production (e.g. in the electric arc furnace) or sold as a by-product for which there is a high demand in applications such as production of ferrites, pigments, refractories and ceramics. The iron oxide obtained by this recovery process is very pure and achieves top prices in the market.

Process enhancements achieved

Recent developments in fluidised bed technology have been patented, as the design of a revolutionary reactor bottom avoiding or minimising shut down periods caused by problems related to the nozzles and the fluidised bed. Usually, a fluidised bed plant has to be shut down periodically as the bed becomes increasingly inhomogeneous due to changes in the nozzle

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configuration (blocking or breaking of nozzles made of heat resistant steel), which compromises fluidisation of the bed. When this occurs, the reactor has to be allowed to cool down fully so that inspection of the nozzles can take place either from the wind box or from inside the reactor, these being particularly unpleasant working conditions. The repair or exchange of nozzles is extremely difficult and the outage time required for repair is a minimum of four days for a small plant, but may require 10 days for large reactors. This requires a massive tank farm to store untreated pickle liquor or a shut down of the pickling line resulting in loss of production of pickled strip.

The new design of the reactor bottom allows nozzles to be examined and individual nozzles to be easily replaced. Even if the full reactor bottom and the wind box - nozzles and brick lining - need to be repaired, an exchange bottom, which has been previously overhauled in the workshop, can be used to replace the worn bottom. The duration of an exchange is in the order of hours and does not require the reactor to be fully cooled down so the plant can be back in operation within a day avoiding the need to slow down or even stop the pickling line.