AN INTEGRATED APPROACH FOR HCL AND METALS RECOVERY FROM WASTE PICKLING SOLUTIONS: PILOT PLANT DESIGN AND OPERATIONS

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Abstract: Pickling is one of the key steps in the hot-dip galvanizing process, where HCl solutions are largely used to remove metal oxides from metallic surfaces, thus generating spent waste liquors containing high concentrations of metals and acid. Disposal of the industrial pickling waste dramatically affects the hot-dip galvanizing industry economics and environmental footprint. Thus, reducing strong acid waste disposal is one of the most beneficial steps to enhance the process sustainability.

Moreover, the continuous regeneration of pickling solutions enhances pickling rate and process performance, also minimizing industrial wastewater disposal and chemicals consumption promoting the circular use of such raw materials.

In this work we propose the recovery and recycling process of valuable substances (e.g. acid, metals and aqueous streams) from pickling solutions by coupling two innovative cutting-edge membrane technologies: diffusion dialysis (DD)[1] and membrane distillation (MD)[2].

A pilot-scale unit was designed and build following extensive experimental and simulative campaigns carried out the ReWaCEM project[3]. The Demo system consists of a DD module, where HCl is recovered from the waste pickling acid solution, a MD module, where the recovered HCl is concentrated, and a reactive precipitation section, where Fe ions, exiting with the metals-rich retentate brine from the diffusion dialysis, is recovered as iron hydroxide. In this latter stage, also an ammonium hydroxide/zinc chloride solution is produced, to be reused in the fluxing bath of the hot-dip galvanizing plant.

The fully-automatized pilot unit is able to operate in continuous, guaranteeing the operation at the optimal pickling conditions in terms of HCl and Fe concentration. Moreover, the use of waste heat (for MD operation) further contributes to enhance process sustainability.

The main results of the on-site pilot plant operation are presented. Several experiments were carried out to assess the system operability and the feasibility of fully reducing spent pickling solution disposal and recovering valuable materials. Results have shown that high recovery of acid (80%) can be achieved in the Diffusion Dialysis unit since the presence of iron ions in solution further increases

acid recovery, although significant Zn leakage occurs through the membrane. On the other side, the performance of MD is good when operating in the lower range of metals concentration, while it suffers when metal salts are present in large quantities (due to poorer rejection in the DD unit) due to the lower water vapor pressure. On the basis of this first pilot campaign an optimized configuration for the system has been developed and will be tested in the next months.

References

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