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An integrated approach for HCl and metals recovery from waste pickling solutions: pilot plant design and operations

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Abstract: Continuous regeneration of industrial pickling solutions and recovery of valuable materials are implemented in a pilot-scale plant including diffusion dialysis, membrane distillation and reactive precipitation units. The main results of the preliminary assessment of on site operation are presented. Different hydrochloric acid concentration and metals composition were investigated and the performance of the system were analysed in terms of quality of recovered compounds, energy efficiency and environmental footprint.

Keywords: industrial wastewater; acid recovery; membrane technologies

Pickling is one of the key steps in the hot-dip galvanizing process, where HCl solutions are largely used thus generating spent waste liquors containing acids and metals in high concentration. Disposal of the industrial pickling waste dramatically affects the hot-dip galvanizing process economics and environmental footprint. Thus, reducing acid waste disposal is one of the most beneficial steps to enhance the process sustainability.

Continuous regeneration of pickling solutions enhances pickling rate and process performance, but also minimises industrial wastewater disposal and chemicals consumption. The recovery and recycling process of valuable substances (e.g. acid, metals and aqueous streams) can be accomplished by coupling two important cutting-edge membrane technologies: diffusion dialysis (DD) and membrane distillation (MD) [1,2]. A demonstration pilot-scale plant was purposely designed and build as a final outcome of 2 years modeling and experimental activities carried out within the EU-H2020 funded ReWaCEM project [3,4]. The Demo plant consists of a DD unit, where HCl is recovered, an MD unit, where HCl is concentrated and fresh water recovered, and a reactive precipitation unit, where Fe, trapped in the outlet solution from the diffusion dialysis, is recovered as iron hydroxide, which is a valuable product. As a by-product, also an ammonium hydroxide/zinc chloride solution is produced, useful in the fluxing bath of the hot-dip galvanizing plant. A schematic of the developed process is reported in Fig. 1.

The pilot unit is able to operate in stationary mode and guarantee the continuous regeneration of the pickling solution at the optimal conditions in terms of HCl and Fe concentration [3]. Moreover, also a recovery of waste heat (necessary for the MD operation) is performed, thus contributing to enhance process sustainability.

In the present work, the results of the first assessment of the on site operation of the pilot plant are presented. Several experiments were carried out to test the Demo operation and assess its performances in terms of materials recovery and energy efficiency, aiming at dramatically reducing spent pickling solution disposal and recover valuable materials.

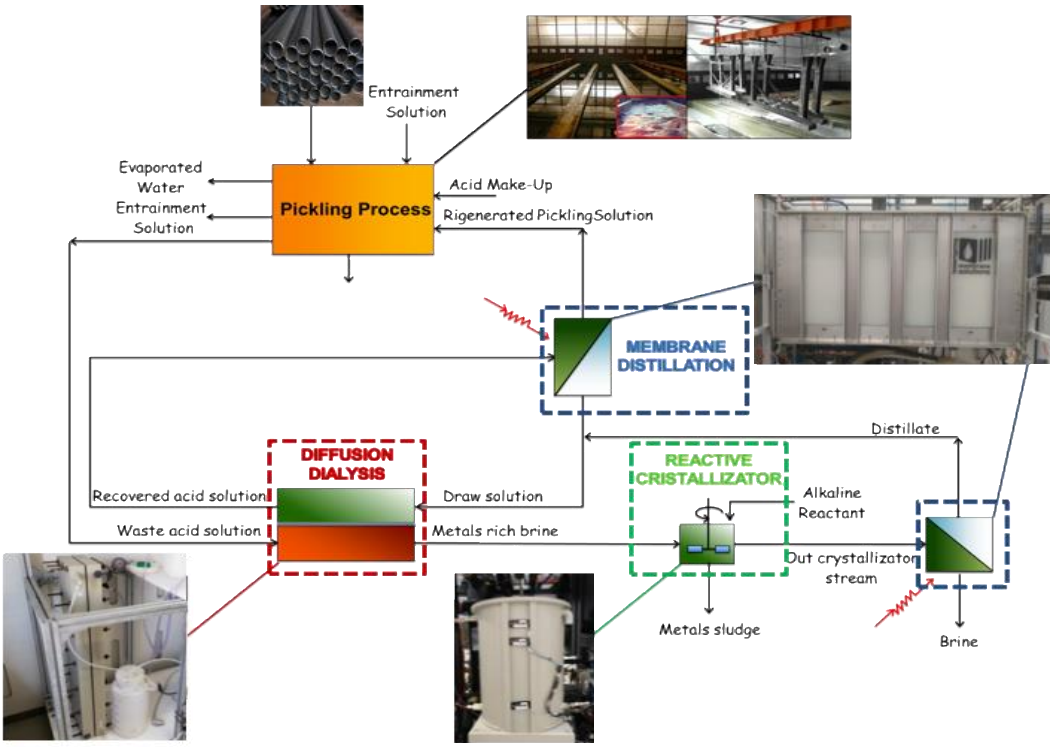

Figure 1 Schematic representation of the developed process, with inset pictures of the single units constituting the pilot plant.

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