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Recovery of metal sulphates and hydrochloric acid from spent pickling liquors

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A R T I C L E I N F O

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A B S T R A C T

Spent pickling liquors are classified like hazardous materials due to their high concentration of metals and presence of different acids and several best available technologies are developed to treat this kind of wastes. In this paper a new process combining essentially the evaporation and crystallization section is developed to produce respectively the aqueous solution of hydrochloric acid and iron-zinc sulphate-eptahydrates, the first used in the same process of pickling while the second to produce fertilizers. The innovative aspect is that two heat pumps are used in replacement of industrial boilers: in literature there are not works about the use of heat pumps for regeneration of spent pickling liquors. Several advantages are obtained in this way: the reduction on ton of equivalent petrol, equal to 39%, and air pollutants, in particular carbon dioxide equal to 59%, according to the European Union climate package. A simulation and an eco-friendly and energy efficient design of the process is carried out. Then an anova analysis to find the influence of several factors on energy efficiency and production of chemical composts is developed. The results show that the optimal operating parameters are following; for evaporation section: pressure 0.2 bar and temperature 357 K; for de-oiling section: outlet temperature 333 K; for the crystallizer section: dissolver temperature 308 K, evaporator and crystallizer temperature 303 K, evaporator pressure 0.03 bar, recycle ratio of mother liquors to evaporator 0.1, evaporator recirculation flowrate 9000 kg/h. This eco-innovation will provide a simple, economic and environmental solution to a problem about management of special hazardous waste. The future construction of the plant will verify the obtained results.

1. Introduction

In the last phase of steel production, metals are rolled and subsequently annealed to achieve the desired properties and structure. The annealing processes occur in presence of air that creates a film of chromium oxide (Cr_2O_3), iron oxides (FeO) and manganese oxide (MnO) on the steel surface. Pickling processes, that consist essentially in acid baths, are made to remove these oxides from metal surfaces, in order to prepare steels for subsequence stages of processing. Typically, HCl and H_2SO_4 solutions are used to treat steels, while for carbon steels mixtures of HNO_3 and HF solutions are utilized. In pickling solutions, inhibitors are also added to reduce the aggressiveness of acids towards the metals. Such pickling solutions are considered exhausted when the acid concentration decreases of 75–85%, while the content of metals also increases up to 150–250 kg/m^3, with a consequent reduction in pickling rate. It is estimated that around $3 \cdot 10^5$ m^3/year of exhausted baths are produced in European Union (EU), with an average metal content of about 40–45 kg/m^3 (Rögener et al., 2012). Accordingly, the amount of spent water generated in these lines is about 10 m^3/h, with an average metal concentration of 0.5–1.5 g/l. Stocks et al. (2005) report the composition of different exhausted pickling baths. Due to corrosive nature and high concentration of acids and metals, the exhausted baths are considered special hazardous wastes (Dahlgren, 2010).

The increasingly stringent regulations regarding the discharge of acids and metals and the growing attention to concepts of regeneration/recycling/reuse of these effluents have focused the interest of the research community towards the development of new technologies called “near zero discharge” (Agrawal and Sahu, 2009). All process flows are then recycled and reused with the aim to not produce wastewaters and to reduce the amount of chemicals (make-up). The regeneration of acids from the pickling

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baths allows several benefits: the reduction of hazardous gases emissions, the improvement of product quality, the increase of pickling rate and environmental responsibility, compatibility with the principles of best available technology (BAT) (Regel-Rosacka, 2010).

Techniques for regeneration of spent pickling solutions include methods with acid recovery, such as diffusion dialysis, electrodialysis, membrane electrolysis and membrane distillation, evaporation, precipitation and spray roasting as well as those with acid and metal recovery: ion exchange, retardation, crystallization solvent and membrane extraction (Agrawal and Sahu, 2009).

The best available techniques are electro-dialysis, diffusion dialysis and crystallization; however spray roasting and retardation/ion-exchange are applied most frequently for regeneration of spent pickling solution (Sinha et al., 2014).

In this research a new process which operates a regeneration and transformation of spent pickling liquors to produce an aqueous solution of hydrochloric acid (18–22% w/w) and iron and zinc sulphate-eptahydrate through a stage of evaporation and crystallization is proposed. The HCl solution is reused in the pickling baths, while the salts can be used as fertilizers as additive or directly in agriculture. The process also involves the use of two heat pumps that allow to exploit the waste heat: in literature there are not works about the use of heat pumps for regeneration of spent pickling liquors and this process is innovative because allows to obtain simultaneously the production of fertilizers and hydrochloric acid from special hazardous waste.

Furthermore, the use of heat pumps respect to a boiler, allows the reduction of primary energy, operating costs and CO_2 emissions, according to EU climate package norms. The advantages of heat pumps respect to traditional systems is also reported in literature by Nitkiewicz and Robert (2014) and Zottl et al. (2011).

In addition a sensitivity analysis using the principle of factorial experiments is carried out to study the process and to find the optimal conditions. The process represents a concrete example of waste management that will meet both the needs of steel and fertilizer industry, using the best technologies for the environment. The implementation at industrial scale in the future and so the experimental data will allow to check the obtained results.

2. Processes to treat spent pickling liquors

Today recovery and energy efficiency are important issues for industry. From the economical point of view, plants tend to reuse as much chemicals as possible, because the unused or free acid in spent baths means the loss of chemicals and potential hazard to natural environment. The ideal solution of waste problem is the application of a “near zero discharge” technology. All the streams in the process are recycled and utilized as much as possible, to produce no wastes (Regel-Rosacka, 2010). The same reasons are for energy efficiency of the process. In literature several technologies about the treatment of spent pickling liquors are reported. Regel-Rosocka (2010) reports a classification of technologies to treat exhaust pickling solutions and highlights the advantages and disadvantages of each technologies. Among them Stocks et al. (2005) report that spray roasting requires high amount of energy to produce a low value product (hydrochloric acid), making this process not economically feasible. This technology is feasible only in systems that allow the regeneration of acid with flows higher than 2–4 m^3/h and it has been also adapted for the regeneration of mixed acids from stainless steel pickling (HNO_3/HF) in so-called Pyromars process (Rögener et al., 2012).

Another technologies used in the treatment of spent pickling baths are processes of neutralization/precipitation with lime (10–15% suspension) or NaOH/KOH; probably the oldest method proposed for SPS processing is the precipitation applied still in many, particularly small, hot-dip galvanizing plants.

Regarding the membrane processes, Regel-Rosacka (2010) reports the advantages and disadvantages. Rögener et al. (2012) show that membrane electrolysis allows to recover nickel from spent pickling acid (minimum 30%). Membrane distillation is studied by Tomaszewska et al. (2001). Nanofiltration is studied by Boricha and Murthy (2009). García et al. (2013) develop an eco-innovative process able to selectively separate the Zn and Fe impurities with the use of commercial hollow fiber membrane modules.

Another studied technology is the use of ion exchange resins, used for recovery of pure salts. Csicsovszki et al. (2005) combine ion exchange resins with electro-winning membranes to recover HCl and to separate Fe from Zn in plating baths. Ione exchange resins are used in Metsep process (Regel-Rosacka, 2010), in RECOFLO acid purification system, in KOM paret retardation system (Miesiac, 2005) and APU technology (Sengupta, 2007). Thanks to its simplicity, space-saving, easy to feasibility and low cost, this technology is mainly used for recovery of acid mixtures from the exhausted baths (Dahlgren, 2010).

Even the solvent extraction is taken into consideration by several authors. Benedetto et al. (2005) propose a new method to recover HNO_3/HF by solvent extraction, using HCl or H_2SO_4 to form metal complexes (Fe (III), Ni (II), Cr (III)), while the acid mixture is extracted by TBP (70%) in iso-paraffin and then stripped with water. Regel-Rosacka (2010) and Regel-Rosocka et al. (2005) propose different scheme for recovery of acid from exhausted baths which provide the reduction of Fe (III) to Fe (II). Manish et al. (2012) observe that copper is completely extracted from exhausted baths by an organic phase containing 30% of Versatic 10 acid at pH 5 (phase ratio of 1:1), while the extraction of the zinc occurs at pH greater than 5. They also find that zinc can be extracted with Cyanex 272 at pH values lower than those used for the extraction of copper. In addition several authors report the removal of Fe and/or Zn by EPT using different extractants such as $(PJMTH^+)_2(SO_4^{-2})$ ionic liquid (Alguacil et al., 2010), DP8R, Acorga M5640 (Gonzalez et al., 2010) and tributylphosphate (Carrera et al., 2009; San Roman et al., 2012).

Crystallization processes are used in the treatment of exhaust pickling water also. This technique allows to recover salts and acid and the last one can be re-circulated. Ozdemir et al. (2006) consider the crystallization as an efficient method to remove ferrous chloride from waters off pickling with hydrochloric acid. However, their studies are based on simulations and have not yet been validated. Kerstin and Rasmuson (2007) build a pilot plant with a continuous crystallizer to recover metals from exhausted baths and HNO_3/HF acid mixture. Kerstin and Rasmuson (2010) develop another crystallization process to treat pickling water containing Fe (III) and Cr (III) depleted ions. The mixture of regenerated acids (HF/HNO_3) is re-circulated, while Cr (III) $F_3 \cdot 3H_2O$ (iso-structural with $CrF_3 \cdot 3H_2O$ and α-$FeF_3 \cdot 3H_2O$) and β-$FeF_3 \cdot 3H_2O$ are precipitated. They also find that the speed of crystal growth is influenced by the presence of Cr. Galvez et al. (2007) study crystallization processes for recovery of HF and HNO_3 from exhaust bath. They develop a model for $K_2FeF \cdot 5H_2O$ and $CrF_3 \cdot 2H_3O$ crystallization by population balances and they find that the growth rate is linearly dependent on the crystal size. Hermoso et al. (2005) develop a crystallization process to recover HF and HNO_3 and to obtain the separation of metals as fluorides from water stripper off. They find that the best operating conditions for the crystallization of $K_2FeF \cdot 5H_2O$ and $CrF_3 \cdot 3H_2O$ are: 333–338 K, pH 4.1–4.2, free HF concentration equal to 14–15% w/w. The process also provides recovery of nickel with yields higher than 72% and a purity around to 100%. Furthermore, Kehrmann (2006) patents a process for the production of iron sulphate heptahydrate from waters off pickling that contain $FeCl_2$, HCl, H_2O. Brown and Olsen