Recovery of the Metals from Pickling Liquors of Stainless Steel by Precipitation Methods

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Pickling liquors are still one of the main environmental concerns of the stainless steel industry. Most of the processes designed to recover these wastes focus on the recovery of their acid content (mixtures of HF and HNO₃), but also produce metals (iron, nickel, chromium and molybdenum) as a low quality by-product that sometimes must be treated as a residue. This paper presents the development of a process to obtain commercial products from the metal content of these liquors. To this end, three precipitation methods (total, sequential and modified) were tested. The proposed procedure is the last one, i.e., modified precipitation. It consists of two stages each resulting in the recovery of solids. The first product is mainly composed of iron and chromium hydroxides and oxides, along with molybdate, while the second is mainly composed of nickel hydroxide. In addition, this method allows an almost total recovery of the acids.

KEYWORDS: stainless steel; pickling; environment; metals; recovery; precipitation.

1. Introduction

Pickling liquors are one of the main environmental concerns of stainless steel producers due to their high content of metals and acids and the complexity of their composition. One additional problem for their treatment is that the acids are in the free form or bonded to the metals, especially hydrofluoric acid with an average concentration of 50 g/l as fluoride complexes and 30 g/l as free acid.

Currently, there are several commercial processes available for the treatment of pickling liquors to recover the high economic value of the acids and the dissolved metals. Most of these are devoted to acid recovery. The methods based on acid retardation recover only the free acid content, producing a residual effluent with a high metal content that is treated by neutralisation. The Aquatech process uses electrodialysis methods to recover free and complexed acids, but the liquor has to be neutralised previously to eliminate the metal content and to avoid membrane fouling. The OPAR process recovers the total acid content by HF/HNO₃ evaporation after spent pickle solution treatment with H₂SO₄, iron and chrome are precipitated as jarosite and it only recovers part of the nickel. With these three procedures the metal cakes are treated as a residue which has to be dumped in landfills. This means a double cost for the companies: the fee they must pay for its disposal and the economical loss of the metals.

The Pyromars process treats the waste by pyrohydrolysis and the Kawasaki process is based on solvent extraction of acids and Fe⁺³, while the remaining Ni and Cr are precipitated as hydroxides by adding alkali and then subjected to a ferrite formation process to produce ferromagnetic compounds. In both cases the acid and metals are recovered, but the operating costs are very high, preventing its use for small companies.

This paper presents the research of three precipitation methods to obtain the metals in different valuable solids. This work was enclosed in the BRIT-EURAM III project “Novel Process to Recover By-Products From Stainless Steel Pickling Baths” (PIBARE Project, BRPR-CT97-0407) carried out by three research centers (National Center for Metallurgical Research and Complutense University of Madrid in Spain and TNO Industrial Research in The Netherlands) and four industrial companies (Tecnicas Reunidas, S.A. in Spain, Outokumpu Steel Oy in Finland, AST in Italy and Vecom Nederland B.V. in The Netherlands).

The aim of this project is to propose an overall process to recover free and complex acids and metals as well as the corresponding rinse water. Conceptually, the process can be divided into the steps shown in Fig. 1. Therefore, the metals recovery step must fulfill the following conditions:

1. An initial stage of free acid recovery by diffusion dialysis, acid retardation or electrodialysis is necessary.
2. The process must recover the highest possible amount of metals, breaking the metal–acid complexes and keeping the acid released in solution to be recovered in a later stage.
3. The metal compounds should be as pure as possible, avoiding the impurities of fluorides and nitrates.

This paper summarises three precipitation procedures (total, sequential and modified ones) studied to fit these aims.
2. Materials and Methods

2.1. Raw Materials

The HNO₃/HF spent liquors were prepared by dissolving 304 stainless steel plates (20×30×10 cm²) in acid solutions (120 g/l of HNO₃ and 30 g/l of HF). In order to maintain the acid concentration, continuous additions were necessary until the metal concentration reached the level of spent liquors. Finally, the molybdenum content was adjusted by the addition of MoO₃ (reagent grade). The liquor concentrations thus obtained are summarised in Table 1.

2.2. Testing Equipments.

Two experimental installations were used for the research. The first one was used for total and sequential precipitation studies. It consisted of a covered spherical reactor made of glass with five holes, two in the reactor body for measuring pH and temperature and three in the cover for the stirring axis, the addition of the basic agent and sampling. Heat was provided by an electrical mantle heater.

The second one was used for modified precipitation (Fig. 2). It consisted of a 2-litre cylindrical reactor with three inlets on the top for the addition of spent liquor and alkali and for a pH-electrode. There was an outlet at a volume of 1,800 ml for continuous sampling. The reactor was placed in a thermostatic bath over a magnetic stirrer.

2.3. Experimental Procedures

Total precipitation. The pickling liquor (V=750 ml) was stirred at the pre-established speed and heated to the required temperature. When the desired temperature was reached, the basic agent was gradually added to obtain the desired pH value. When the pH was stabilised, the reaction condition was maintained for 30 min controlling the pH by small additions of alkali. The product was filtered and washed out three times in the filter. The filtercake was dried at 105°C for 24 h.

Sequential precipitation. The reaction consisted of four precipitation steps at pH 3, 5, 7 and 9. The experimental procedure for each stage was the same as that for total precipitation. In this case, the initial volume of pickling liquor was 500 ml. The filtrate from each stage was introduced again in the reactor and the next step begun.

Modified precipitation. This method consisted of the addition of pickling liquor and an alkali into an initial volume of water, keeping the pH constant. Then, the volume in the reactor was continuously increased until it reached an outlet. Samples were collected at fixed times and analysed.

2.4. Analysis

The precipitates were studied by X-ray diffraction (XRD), using a Siemens D500 diffractometer with CuKα monochromatized radiation, to determine their mineralogical composition. The chemical composition was analysed by X-ray fluorescence (XRF). The analytical procedure involved the preparation of compacts of samples supported on Teflon. Analyses were carried out using a Philips PW1404 FRX spectrometer.

The metal concentrations in the filtrate were determined by atomic absorption spectrometry (AAS) by using a VARIAN SpectrAA 220 spectrophotometer. The fluoride and nitrate contents were determined by ion chromatography (IC) by using a VARIAN SDS 9002 pump, a HAMILTON PRP X-100 column and a METROHM 732 conductivity detector.

3. Results and Discussion

3.1. Total Precipitation

Total precipitation is the usual treatment of pickling liquors or effluents from acid recovery processes based on retardation resins or membrane techniques. The classical operation is designed to obtain a clean effluent that satisfies the environmental regulations, removing the metal content in solution and producing a solid with all the potential pollutants. The aim of this part of our research is to improve this operation so that it suits it in the overall process shown in Fig. 1. This implies that the effluent has to contain the highest possible amount of anions to be recovered in a later stage, while the solid has to be anion free for its recycling.

The variables studied were: alkali concentration, pH, temperature and KF as an alkali additive. The alkali used in all experiments was potassium hydroxide. Table 2 shows the variables and conditions used in the study. The results of effluent and solid composition after precipitation are...
shown in Table 3. When the lowest alkali concentrations were used (Tables 2 and 3, experiment 1), a very diluted filtrate with a large volume was obtained, which made a successive step of pre-concentration necessary to close the water balance of the process described in Fig. 1. This implied higher costs. On the other hand, it maintained a higher metal concentration of metals in solution, avoiding the segregation of the effluent without a previous refining stage. Both effects were diminished when the alkali concentration was increased to 6 or 10 molar or when a combination of 1.5 and 10 M solutions was used (Tables 2 and 3, experiments 2–5). In these experiments, the solids obtained were a mixture of iron and chromium fluorides and oxides, along with molybdate and nickel hydroxide. Therefore, the solids had a high fluoride content that prevented their possible recycling. When KF was used as an additive (Tables 2 and 3, experiments 6–8), the precipitates were mainly composed of iron, chromium and nickel oxides or hydroxides, and molybdate. This indicated that the use of potassium fluoride as an additive modified the reaction mechanism.

Table 3. Composition of filtrate (g/L) and filtercake (%) from total precipitation experiments.

| EXP | Conc. | Fe | Ni | Cr | Mo | K | F | NO3 | V (ml) |
|-----|-------|----|----|----|----|---|----|-----|--------|
| Initial | 44.63 | 4.38 | 6.94 | 1.28 | --- | --- | --- | 34.24 | 91.08 |
| Final | 0.170 | 0.005 | 0.040 | 0.040 | 0.10 | 42.56 | 11.3 | 134.5 | 1850 |
| Initial | 44.08 | 5.78 | 7.81 | 1.33 | --- | --- | --- | 33.19 | 151.06 |
| Final | 0.003 | 0.030 | 0.081 | 0.19 | 43.0 | 7.8 | 33.5 | 1210 |
| Initial | 44.26 | 4.15 | 11.43 | 1.18 | --- | --- | 55.9 | 146.98 |
| Final | 0.005 | 0.005 | 0.009 | 0.066 | 113.0 | 26.8 | 90.5 | 570 |
| Initial | 43.35 | 5.45 | 10.45 | 1.04 | --- | --- | 56.82 | 119.92 |
| Final | 0.004 | 0.007 | 0.015 | 0.051 | 125.1 | 30.8 | 75.2 | 600 |
| Initial | 44.15 | 4.96 | 10.33 | 1.12 | --- | --- | 71.8 | 145.8 |
| Final | 0.001 | 0.008 | 0.015 | 0.036 | 92.3 | 31.6 | 50.4 | 490 |
| Initial | 44.31 | 4.56 | 10.89 | 1.06 | --- | --- | 60.32 | 136.25 |
| Final | 0.001 | 0.016 | 0.083 | 0.68 | 138.9 | 38.60 | 66.8 | 330 |
| Initial | 43.85 | 5.33 | 10.54 | 1.19 | --- | --- | 48.56 | 150.10 |
| Final | 0.009 | 0.003 | 0.011 | 0.062 | 80.6 | 11.5 | 72.2 | 650 |
| Initial | 43.66 | 5.27 | 10.23 | 1.24 | --- | --- | 51.24 | 140.82 |
| Final | 0.007 | 0.003 | 0.006 | 0.104 | 73.6 | 10.0 | 80.1 | 730 |
| Initial | 43.20 | 5.57 | 10.87 | 1.14 | --- | --- | 28.78 | 138.38 |
| Final | 0.006 | 0.016 | 0.041 | 0.715 | 119.2 | 27.24 | 80.0 | 580 |

| EXP | T | K | Cr | Mn | Fe | Ni | Mo | Others |
|-----|---|---|----|----|----|----|----|--------|
| 1 | 11.0 | 4.2 | 9.9 | 0.84 | 39.1 | 4.9 | 0.77 |        |
| 2 | 10.5 | 3.6 | 10.0 | 0.83 | 39.7 | 4.9 | 0.83 |        |
| 3 | 11.9 | 6.9 | 9.4 | 0.78 | 37.5 | 4.6 | 0.52 |        |
| 4 | 7.8 | 21.3 | 7.1 | 0.61 | 26.6 | 3.4 | 0.36 | 6.4 |
| 5 | 4.0 | 3.3 | 10.9 | 0.95 | 34.3 | 5.5 | 0.45 |        |
| 6 | 2.5 | 2.5 | 13.4 | 0.99 | 42.5 | 5.8 | 0.54 |        |
| 7 | 14.2 | 9.2 | 8.9 | 0.75 | 35.3 | 4.3 | 0.40 |        |
| 8 | 0.9 | 5.1 | 10.9 | 0.96 | 44.3 | 5.6 | 0.12 |        |

Fig. 3. Reaction mechanism of precipitation of HF/HNO3 liquors.
tion steps and KOH 1.5 M in the last one. Table 4 shows the filtrate compositions for each stage. Almost all the initial content of Mo was precipitated at the first stage. In order to avoid the re-dissolution at a higher pH the solid was removed. Nevertheless, good separation of the metals into different solids was not achieved. The precipitates were mixtures of different compounds of all the metals, presumably due to massive precipitation. Therefore, the most profitable way was to precipitate the first solid with the highest possible amount of Fe, Cr and Mo, keeping Ni in solution to be separated by posterior processes.

The best recuperation rate was reached at pH 7 using KOH as alkali, but the highest purity was obtained by using NH₄OH/KOH at pH 7. In this case, the dosage of EDTA/Ni=1 (molar ratio) resulted in 10% more dissolved Ni than a dosage of 0.5. In contrast, using only KOH as alkali at pH=7, the Ni stabilisation was very similar, but at pH=9 the higher dosage partially prevented the precipitation of the metal. In addition, using ammonia at pH=9, the purity of Ni solution was close to 90%.

During the study with NTA, it was observed, on one hand, that a 0.5 ratio effected higher stabilisation of Ni and, on the other hand, the precipitation of the solution until pH=9 implied an important loss of dissolved Ni. The best results were obtained using KOH at pH=7, and the purity of the Ni dissolved in these conditions was higher than 90%.

In summary, the use of complexing reagents largely improved the final results. The best results with EDTA were attained at pH 9, using NH₄OH/KOH at a ratio of 1. On the other hand, working with NTA, the best results were achieved at pH 7 with KOH. Bearing in mind that both binders have similar costs and the higher price of ammonia compared to KOH, the results indicate that the optimum conditions are precipitation with NTA and KOH at pH 7.

Table 4 shows the concentration of fluoride and nitrate after each precipitation step. In non-complexing reagent reactions, similar nitrate recovery was observed for both alkalis. This amount was about 75%. For fluoride, ammonia obtained higher concentrations than KOH, but this recovery was never higher than 20%. This effect was greater when any organic binder was used, e.g. a dosage of EDTA/Ni=1, using KOH as alkali, the anion recovery was less than 10% of F⁻ and 60% of NO₃⁻. In contrast, when ammonia was used, the same recovery was obtained as with no binder. With NTA, the results were lower, e.g., when the dosage of NTA/Ni=0.5 was used, the final recovery was less than 15% of F⁻ and 50% of NO₃⁻.

An important factor for the feasibility of this process is the recovery of the complexing reagent. Since large amounts of it are required, along with the environmental restrictions of their use and the low recovery of anions, this alternative process would not be feasible.

3.3. Modified Precipitation

This procedure was designed to take advantage of the knowledge gained from the reaction mechanism described in the total precipitation procedure. It was possible to separate the total content of Fe and Cr as K₃MF₆ at low pH if further free fluoride was added. In addition, the total Mo content was precipitated as molybdate. If the solid is removed from the solution, it is possible to get a solution mainly composed of Ni and nitrate that could be precipitat-
ed later to produce nickel hydroxide and a nitrate dissolution. The first solids of hexafluoride could be re-dissolved at a higher pH and then precipitated again as Fe and Cr hydroxides. The fluoride would be released and maintained in solution to be mixed with the former stream of nitrate. This effluent would be fed to the next stage of anion recovery. To avoid massive precipitation, the spent liquor and the alkali were fed over an initial volume of water. In this way, the precipitation was produced in a more diluted media. The experimental process consists of two series of conditions as given in Table 5. The first one (tests 1–10) was carried out with synthetic liquors prepared by dissolving metal salts and acids up to the composition of spent pickle solutions. The results of this first block of tests are shown in Fig. 5. The best pH interval was between 3 and 4. At lower pH no metal precipitates were generated, while at higher pH the almost total precipitation of all the metals was achieved. Under these pH ranges, it was possible to precipitate 99.5% of Fe and Mo, but keeping 75% of Ni in solution. The use of ammonia caused unfavourable separation of the metal, because it stabilised the metals in solution. The influence of the initial water volume was not significant, but the lower volumes showed better results. The results of the second series (Table 5, tests 11–13) are shown in Fig. 6. It can be seen that the influence of temperature was very important. At 80°C, Ni remained in solution while most of the other metals were precipitated. The

Table 5. Experimental conditions of modified precipitation tests.

| TEST | pH | Alkali | Temperature (°C) | Initial water volume (ml) |
|------|----|--------|------------------|--------------------------|
| 1    | 1  | NaOH 20% | Room          | 100                      |
| 2    | 2  | NaOH 20% | Room          | 100                      |
| 3    | 3  | NaOH 20% | Room          | 100                      |
| 4    | 4  | NaOH 20% | Room          | 100                      |
| 5    | 5  | NaOH 20% | Room          | 100                      |
| 6    | 3  | NaOH 20% | Room          | 1000                     |
| 7    | 4  | NaOH 20% | Room          | 1000                     |
| 8    | 1.5| NaOH 20% | Room         | 100                      |
| 9    | 3  | NH₄OH 25%| Room         | 100                      |
| 10   | 4  | NH₄OH 25%| Room         | 100                      |
| 11   | 4  | KOH 1.5m | Room         | 100                      |
| 12   | 4  | KOH 1.5m | 80           | 100                      |
| 13   | 3.5| KOH 1.5m | 80           | 100                      |
amount of Ni stabilised in this way ranged between 50 and 90% of the initial metal. At pH 4, the concentration of Fe, Cr and Mo in the effluent was very low (about 5%), but the Ni in solution to be recovered was 55% of the initial concentration. On the other hand, at pH 3.5, the concentration of Fe, Cr and Mo was higher than at pH 4 (between 5 and 15% of the initial concentration), but about 85% of the initial Ni was kept in solution. At the latter pH, Fe and Cr were precipitated as K\(_3\)FeF\(_6\) and K\(_3\)CrF\(_6\), but the problem was that fluoride was in stoichiometric deficit with respect to the concentration of Fe+Cr. Therefore, part of these elements were kept in solution. If supplementary amounts of fluoride, as HF or KF, were added, the total content of Fe and Cr could be precipitated.

The effluent of this first precipitation composed of Ni and nitrate could be precipitated (pH between 7 and 9) to obtain Ni(OH)\(_2\), leaving the nitrate in solution.

The K\(_3\)MF\(_6\) compounds could be re-dissolved to recover the fluoride content. Then, the Fe and Cr could be precipitated at higher pH (≈5) in a second operation. The effluent of fluoride solution could be mixed with the stream of nitrates to be recovered in the form of hydrofluoric and nitric acids. A possible flow diagram of the overall process is shown in Fig. 7.

4. Conclusions

From a technical point of view, the best alternative is the modified precipitation as it allows the recovery of two solids. The first one would be composed of Fe, Cr and Mo as hydroxides and salts, while the second one would be mainly nickel hydroxide. This method also allows the recovery of the acid content. From an economical point of view, the actual costs for the disposal of solids like those obtained from total precipitation make this procedure not feasible due to the higher installation and operation costs. Nevertheless, when the environmental policy becomes more restrictive in a near future concerning the type of wastes to be disposed and the much higher fees, this process will be economically attractive.

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