

COMMUNICATION

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RECOVERY OF CHROMIUM ON ION EXCHANGE UNITS

A number of procedures have been described for purifying acidic wastewaters from hexavalent chromium. One of the most frequent methods consists in reduction of Cr^{VI} to Cr^{III} followed by neutralization and separation of chromium^{III} hydroxide. The main disadvantage of this process, apart from the difficulties with sludge thickening, is that resulting semi-solid waste cannot be recycled under economic conditions.

The procedures which make use of ion exchange units are based on a very efficient sorption of hexavalent chromium on anion exchange resins [4], thus enabling a selective removal of most anions. The affinity of anions to the functional groups of strongly basic anion exchange resins decreases [1] in a series $\text{Cr}_2\text{O}_7^{2-} > \text{CrO}_4^{2-} > \text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^- > \text{OH}^-$. Regeneration by elution with alkalis (mostly NaOH alone or with additives) has to be performed using a large excess of the regenerating solution. This leads to the dilution of the regenerate; its concentration reaches 4–6% of Na_2CrO_4 only. This is a consequence of low affinity of functional groups to hydroxyls. Chemical stability of the anion exchange resins towards hydrolytic or oxidation processes makes another critical point of this procedure. Strongly basic anion exchange resins are known to degrade in alkalis their functional groups because of their decomposition. This leads, especially in concentrated solutions of alkali hydroxides and at elevated temperatures, to substantial losses in exchange capacity. Such danger is more pronounced if oxidants are present. The weakly basic anion exchange resins are more stable towards alkalis, they are, however, apt to easy oxidation, especially in contact with acid wastewaters (under pH 4).

As a contribution to solving such problems related to purification of wastewaters containing hexavalent chromium, a new process has been developed as a joint project of the Ore Research Institute and the Institute of Macromolecular Chemistry. The primary target was to decrease the content of chromium in wastewaters from the production of vanadium so that these waters, after selective separation of Cr^{VI} , could be returned to the technological process. Chromium, in turn, should be recoverable in the form of a concentrate, to be further processed under economic conditions. The typical composition of respective waters was as follows:

- Cr^{VI} — 0.5–2 g/dm³,
- V^{V} — 0.1–0.3 g/dm³,
- SO_4^{2-} — 60–80 g/dm³,
- Na^+ — 30–40 g/dm³,
- NH_4^+ — 5–10 g/dm³,
- silicates as SiO_2 — 0.5–1 g/dm³,
- Fe, Mn, Ti, Al — under 0.1 g/dm³.

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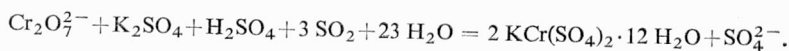
As a good selectivity was first aimed at the use of ion exchange resins appeared to be the best choice.

It is well known [3] that the strongly basic anion exchange resins do not adsorb vanadium^V at pH below 2. If the pH value is higher, the sorption of vanadium alone is gradually pronounced but even in this case, in presence of Cr^{VI}, the chromium containing anions are expected to be bound more strongly and, therefore, to displace vanadium gradually to the eluate. This is the principle of the proposed new technology. The wastewaters containing the above mentioned main components are filtered through an anion exchange bed, e.g. in sulphate form. There is absorbed preferably Cr^{VI} with some vanadium content. The latter is, however, eventually displaced by Cr^{VI}, the break-through of vanadium taking place faster than that of chromium. In our experiments with a solution containing 1.24 g Cr^{VI}/dm³ and 0.1 g V^V/dm³ the break-through points for vanadium were recorded at the solution to bed volume ratio equal to 16:1 and 55:1, respectively. With the increasing sorption the amount of the chromium bound per bed volume raises up to the maximum capacity of the ion exchange resin. As the waters in question are fairly acidic, the Cr^{VI} is bound mostly as bichromate which doubles the capacity of the exchanger. The capacities found for the above mentioned strongly basic Amberlyst A 26 and for weakly basic Ostion LG - AWP were 60 and 75 g Cr^{VI}/dm³ of the bed, respectively. Under the operational conditions, it is suitable to use two columns connected in series. In the first one, the maximum capacity for Cr^{VI} is reached, in the second all chromium is separated from water which without any further treatment can be reused for production of vanadium.

As already mentioned, in the so far described procedures using ion exchangers, the regeneration step is a critical point. In these procedures concentrated solutions of alkali hydroxides alone or with additional salts, e.g. sodium chloride, are used as regenerating agent. As the result of high affinity, chromate is so strongly bound to the ion exchanger that an excess of regenerating solution is required to complete the regeneration. Thus, in addition to alkali chromate, the regenerate contains the excesses of hydroxide and all other salts originally present; this regeneration has been found to be more difficult.

On the contrary, the new procedure proposed has high regeneration efficiency due to reduction of Cr^{VI} to Cr^{III} turning chromium into a cation, which is repulsed from the anion exchanger by Donnan forces. In practical realization chromium-saturated anion exchange bed is treated with gaseous sulphur dioxide. The gas is supplied into the column through the nozzles at its bottom. The consumption of sulphur dioxide is nearly theoretical as the reaction proceeds quite smoothly. The resulting concentrated regenerate contains only Cr^{III} and SO₄²⁻ ions with concentration of SO₃²⁻. All chromium is contained in the solution filling the interstitial volume and swelling volume inside the particles. These volumes can be estimated as being at most 30% and 35%, respectively, of the bed volume, the latter value depends on the porosity and/or degree of cross-linking of the ion exchange bed. Hence, the expected chromium concentration can be roughly calculated and, indeed, our experiments showed that regenerates with chromium content of 80 and 90 g/dm³ had been readily obtained with strongly and weakly basic anion exchange bed, respectively. The regenerate can be easily removed from the column by a minimal amount of the diluted sulphuric acid. The concentration of chromium in the eluate is sufficient for further direct processing and, at the same time, the column is ready for the next cycle starting with the sorption step.

High purity of the regenerate together with high concentration of chromium^{III} decides about the modes of further processing. One of the possibilities is the production of chromium alum, KCr(SO₄)₂ · 12 H₂O, according to the following reaction:



As alternatives, direct electrolysis reduction to metallic chromium, anodic oxidation to chromium trioxide, processing to chromium pigments, production of ferrochromium etc. could be considered.

The proposed new way of regeneration is particularly safe, as far as the hydrolytic and oxidation stability of the exchanger is concerned. At any time, the exchanger does not come in contact with alkaline solutions. In the sorption step, the pH is within moderately acidic range, raising during the regeneration, the medium, however, is no longer present; whereas sulphur dioxide protects the exchanger against oxidation even in the stage of the elution with sulphuric acid. Repeated sorption and regeneration cycles, even

after prolonged periods, did not lead to the decrease of capacities of either strongly or weakly basic ion exchangers. It has been also verified that even elevated temperatures (up to 80°C) do not impair the capacities; this is a great advantage as the regeneration is exothermal.

The knowledge acquired when solving the present problems is of a general importance in all branches where hexavalent chromium containing wastewaters have to be purified.

The high regeneration efficiency of the proposed process together with high selectivity of chromium removal in presence of other contaminants favour the procedures using ion exchangers economically, especially when the situation in the supply of chromium ores is critical. At the same time, it is an interesting example showing how the ion exchange technologies are adaptable and how they can help to solve environmental problems. For these reasons a patent application has been filed for the process.

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