

CHROMIUM METAL RECOVERY FROM INDUSTRIAL WASTE WATER

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The problem of chromium [particularly chromium(VI)] compounds in industrial waste water is found in different technical processes. The best known sources of effluents containing chromium ions are chromium plating shops working with electrolytes based on aqueous solutions of chromic acid, metallurgic plants producing or processing alloyed steels (where types with high chromium and nickel content are dominating) and running acidic pickling baths, and – last but not least – factories for vanadium oxide production. The main fraction of vanadium oxide is later converted into ferrovandium and sold to steel industry. The reason for a chromium problem in this process is the (inevitable) chromium content of all available vanadium raw materials.

Waste water streams charged with high amounts of chromate (CrO_4^{2-}) ions are frequently treated with e.g. sulfur dioxide to reduce chromium(VI) to chromium(III) ions which are precipitated in form of chromium(III)-hydroxide or hydrous chromium oxide. The following steps are separation of this water-containing product and disposal. This way is particularly unpopular in Austria because the national resources of chromium containing minerals are negligible and all chromium has to be imported.

All the presently existing technologies to save chromium containing materials and to save money by improved waste water cleaning show severe drawbacks. Electroplaters fight against accumulation of organic pollutants in their electrolyte loops, steelworkers complain that in the case of alloyed steels drying and roasting of pickling residues recovers only the acid or the anhydride of the same. The solid oxides are usually separated in such a complex mixture that there is no economic possibility to recycle them. All the other processes deliver (as mentioned before) hydrated solid chromium(III) compounds which have to be disposed of at particularly designed, equipped and controlled sites resulting in high cost and an inevitable loss of material.

Finally it was recognized that chromium(III) oxide should be regarded as an intermediate on the way to a more refined product. For a certain period of time this “more refined product” was expected to be exclusively metallic chromium which should be electrolytically deposited in a purity of at least 99%. When all the available processes to achieve this goal in principle were reviewed the result was rather disappointing: only one electrolytic production method would be able to maintain the present mass flow without severe problems, namely the electrolysis of a solution of potassium- or ammonium-chromium(III)alum [1].

Nearly all technical processes applying electrolysis of chromium(III)alum solutions documented in the open literature [2,3] or in patents [4,5] are originally designed for another raw material and start with dissolution of ferrochrome in sulfuric acid and recycled

crystallization mother liquors.

It was one of the main targets to adapt one of these processes for a possible use in chromium recovery from waste water. In the original process, elimination of carbon and precipitation of iron as ferrous sulfate ($\text{FeSO}_4 \cdot n \text{H}_2\text{O}$) are necessary. These operations may be left out and they have to be replaced by re-dissolution of the prematurely precipitated hydrous chromium oxide in sulfuric acid to gain a concentrate. The final precipitation step, crystallization of ammonium-chromium(III)aluminum-dodecahydrate [$\text{NH}_4\text{Cr}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$], is the same.

It was observed that crystallization is only possible after transformation of the initial sulfate containing chromium(III)-complex (green solution) to the chromium(III)-aquocomplex (violet or purple solution). The green compounds are more stable above 50 °C and contain ions like $[\text{Cr}(\text{H}_2\text{O})_5(\text{SO}_4)]^+$, $[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ and $[(\text{SO}_4)(\text{H}_2\text{O})_4\text{Cr}-\text{O}-\text{Cr}(\text{H}_2\text{O})_5]^{2+}$. The violet modification is formed in cool, dilute solutions of moderate acidity and contains preferably $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ions [6]. This effect is not welcome because it is time-consuming (up to 24 hours) and it is thus regarded as a critical step in processes with a high mass-flow rate.

As an alternative it was tried to find particular conditions for the electrolytic chromium deposition using an acidic chromium sulfate solution and, as a result, to avoid the whole crystallization procedure. The critical parameters to achieve a tolerable current efficiency and a reasonable grade of metal purity were found to be the choice of the electrode materials, temperature, electrolyte flow rate, concentration of impurities (particularly of iron- and zinc-ions) in the electrolyte.

References:

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