NMFRC
NATIONAL METAL FINISHING RESOURCE CENTER

Pollution Prevention and Control Technologies for Plating Operations

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Section 6 - Wastewater Treatment

6.2 CONVENTIONAL TREATMENT TECHNOLOGIES

6.2.2 Chromium Reduction

Various metal finishing processes contribute chromium to the wastewater. Among these are chromium plating, chromating, bright dipping, chromic acid anodizing and chromium stripping. Although chromium is present in both the trivalent (Cr+3) and hexavalent (Cr+6) state in process solutions and wastes, the dominant species is Cr+6. Unlike most heavy metals which are precipitated readily as insoluble hydroxides by pH adjustment, Cr+6 must first be reduced to the trivalent state because it forms the chromate complex which behaves as an anion and cannot form an insoluble hydroxide (ref. 38).

Conventional chromium reduction is achieved by reaction of Cr+6 with a reducing agent. The most commonly used reducing agents are sulfur dioxide gas and sodium metabisulfite (dry granular power). Alternative reducing agents include: sodium hydrosulfite, ferrous sulfate and iron or steel scrap (ref. 38). The chemical equations applicable to reduction with sulfur dioxide and sodium metabisulfite (actually sodium bisulfite, which is formed when sodium metabisulfite is added to water) are (ref. 38, 413):

Sulfur Dioxide Gas:

3SO2 + 2H2CrO4- ó> Cr2(SO4)3 + 2HOH

Sodium Bisulfite:

3NaHSO3 + 2H2CrO4 + 3H2SO4 ó>

Cr2(SO4)3 + 5HOH + 3NaHSO4

A typical chromium reduction process is shown in Exhibit 6-4. The basic equipment includes a reaction tank, mixer, chemical feed system, pH meter/controller, an oxidation reduction potential (ORP) meter/controller, transfer pumps and level controls.

The type of chemical feed system selected will depend on the reduction reagent selected. Sulfur dioxide gas usage is restricted mostly to large treatment plants and sodium bisulfite is used at most small and medium-sized systems, but it is also used at large systems. Sulfur dioxide gas is the reagent of choice for larger systems due mainly to its lower chemical cost (at high feed rates it is nearly 50% less expensive, see Section 6.3.2). However, its use has drawbacks that cause it to be less desirable for smaller systems; these are: (1) requires a more expensive chemical feed system (sulfonator) and (2) presents a health hazard. The latter of these factors is the result of the toxic nature of sulfur dioxide gas. To overcome the health hazard, many large facilities install a vacuum system to prevent losses of sulfur dioxide to the working area, which further increases the capital cost of using this reagent. The results of the Users Survey indicate that approximately 6% of all respondents use sulfur dioxide and approximately 60% of all respondents use sodium bisulfite (approximately 34% do not have a chromium treatment process or use an alternative chemical). Shops using sulfur dioxide had average and median industrial wastewater flow rates of 153,814 gpd and 55,000 gpd, respectively. For all shops surveyed, the average and median flows were 34,600 gpd and 14,000 gpd.

The efficiency of the reduction reaction is highly dependent on pH (Exhibit 6-5), and most conventional processes are operated between pH 2.0 and 3.0. Since the incoming wastewater is usually above this desired range, sulfuric acid is added to reduce the pH. This is a drawback of the conventional process since the subsequent metal removal step is performed at an elevated pH (typically 7.0 to 9.5), and therefore the introduction of acid increases the subsequent need for alkali reagent.

The conventional chromium reduction processes are capable of producing an effluent with less than 0.1 mg/l Cr^{+6} (ref. 39).

The theoretical quantity of sodium bisulfite or sulfur dioxide required to reduce one pound of hexavalent chromium is approximately 3 lbs and 2 lbs, respectively. One source estimates that 0.2 lbs of sulfuric acid are required to lower the pH to the required range of 2.0 to 3.0 (ref. 392). The results of the Users Survey indicate that actual chemical requirements for chromium reduction and pH adjustment are much greater than the theoretical or estimated quantities presented by most references. In fact actual dosages are often five to ten times or more than theoretical dosages. Treatment chemical usage data from survey respondents is presented and discussed in Section 6.3.2.

The following is a discussion of two alternative methods to the conventional sulfur compound chromium reduction process that are in use by the metal finishing industry: the sacrificial iron anode and sulfate reduction methods.

The sacrificial iron anode technology makes use of an electrochemical reaction in which an electrical current is applied to consumable iron electrodes. The electrochemical cell consists of a number of 1/8 in. cold rolled carbon steel plates separated by 1/8 in. gaps. A DC power supply is connected across the two end plates. Wastewater flows through the gaps in contact with the electrodes allowing the current to flow from electrode to elecärode. The current flow causes the anode to dissolve slowly, thereby generating ferrous ions into the wastewater stream. The ferrous iron chemically reacts with the hexavalent chromium and reduces it to the trivalent state. During this reduction process, the iron is converted to trivalent iron hydroxide which results in a co-precipitation effect, where the iron hydroxide adsorbs heavy metal cations onto its surface (ref. 412). The process has the advantage of able to reduce chromium at neutral pH. A drawback is that the process produces ferric hydroxides, which increases the quantity of sludge (ref. 39). Five respondents to the Users Survey (1.6%) use this technology (PS 083, PS 181, PS 240, PS 244 and PS 300). These systems, which were purchased between 1983 and 1991, were given satisfaction ratings of 3 and 4 (on a scale of 1 to 5, with 5 being the highest level of satisfaction) (three respondents did not provide a satisfaction rating). One of the technology users indicated that they purchase approximately $2,000 of replacement electrodes per year for their sacrificial iron anode unit (PS 083). This shop has a chromium bearing wastewater flow of 8,000 to 10,000 gpd. Another shop purchases approximately 2,900 lbs/yr of iron ($1.35/lb). This shop has a total plating flow of 25,810 gpd.

Ferrous sulfate reduction has been used to reduce chromate in an acid environment for a number of years. The primary advantage for many facilities was an inexpensive, abundant supply of ferrous sulfate, which is a waste product from steel pickling. The disadvantage of the process is the considerable increase in sludge generation owing to the precipitation of ferric hydroxide in the neutralization phase of the treatment. Pilot evaluations during the early 1980ís of alkaline ferrous sulfate reduction of chromate were relatively successful. The process was proven capable of rapid reduction at pH levels between 8 to 10. The advantage of the alkaline process is the savings in sulfuric acid and caustic that are used with the conventional reduction process to lower and subsequently raise the pH. Also, the reduction process can be accomplished in the same reaction vessel as neutralization, which reduces equipment requirements (ref. 39). However, the process still has unfavorable sludge generation characteristics and a lack of control in chemical metering (ref. 348). The use of ferrous sulfate as a hexavalent chromium reducing compound was reported by only two respondents to the Users Survey (PS 020 and PS 135). At least one of those shops performs reduction in an alkaline environment (PS 135). Also, ferrous sulfate is used by approximately 3.1% of all respondents for co-precipitation. Sodium hydrosulfite is also used by one respondent as a chromium reducing agent in an alkaline environment (PS 173 and PS 253). PS 253 treats a 28,300 gpd chromium wastestream containing an average of 68.3 mg/l Cr. This shop uses 12,400 lbs/yr of sodium hydrosulfite in their chromium reduction process.

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