APPLIED CHEMISTRY

Recovery of Chromium from the Solid Residue by In-Situ-Generated Hypochlorite

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The present study provides an electrochemical process for the recovery of chromium value from the solid residue of a chromium plant using electrogenerated hypochlorite. The process was studied using an in situ extraction method. The effect of various parameters—such as pH, concentration of hypochlorite, particle size of the solid effluent, pretreatment of sludge, choice of the acid for pH maintenance, and stirring—on the extraction efficiency of chromium was investigated. A significant portion (50%−60%) of the total chromium content was recovered by performing the reaction under suitable operating conditions with hypochlorite.

Introduction

Chromate and chromium chemicals have extensive applications in the field of pigment products, the processing of leather and textiles, the surface treatment of metal, corrosion control, and the manufacture of other chemical products. Chromate is manufactured from chromite ore via thermal oxidation of the chromic oxide in the ore with soda ash and hydrated lime at 1100 °C. In a continuously working chromate plant, for every 100 tonnes of ore, 65 tonnes of residue is obtained. The residue may be either discarded or used in the next stage, depending on the operating cycle. The production of ∼50 000 TPA of chromium chemicals in India causes exhaustive emissions of chromium, in the form of solid effluents. Over the years, many tonnes of this residue have been dumped in and around these industries, resulting in the leaching of thousands of tonnes of soluble chromium, which pollutes the soil and thereby contaminates the groundwater. The contaminated soil contains chromium in two valance states: viz., a soluble, toxic Cr(VI) form and a less-toxic, insoluble Cr(III) form. It has been established that ∼15% of the Cr(III) species in the soil becomes oxidized to Cr(VI) and contaminates the groundwater. Most of the industries resort to effluent treatment processes to prevent pollution. The effluent treatment processes are based on chemical, biological, and electrochemical systems. It has been well-established that electrochemistry has much to offer, in regard to the prevention of pollution and protection of the environment.[1−25] Electrochemical treatment can exist in two types: (i) the direct oxidation of chromate to chromite and (ii) the conversion of chromium(III) hydroxide precipitated from the effluent and sludge by hypochlorite. It has been reported[26,27] that the oxidation of Cr(III) to Cr(VI) via the electrolytic method has been done in the regeneration of spent chromic acid from organic oxidation reactions. The recovery of Cr(III) from sludge resulting from municipal and industrial waste has been performed by treating the concentrated chromium(III) oxide/

hydroxide with hypochlorite solution. The treatment of solid effluent from chromate-producing industries has not been attempted so far. This paper presents the results of a study on the recovery of chromium value from the solid residue of a chromate plant via oxidation with in-situ-electrogenerated hypochlorite. To optimize the parametric conditions, the effect of various parameters (such as pH, concentration of hypochlorite, particle size of the solid effluent, pretreatment of sludge, choice of the acid for pH maintenance, and stirring) on the extraction efficiency of chromium was investigated.

Materials and Methods

Cell Construction and Electrolysis. The electrolytic cell (Figure 1) consisted of a 0.50-L Pyrex tall glass vessel that had been fitted with a poly(vinyl chloride) (PVC) cell cover (with slots to introduce the electrolyte), a pH sensor, a thermometer, and electrodes. A noble-metal oxide ($RuO_2/TiO_2/SnO_2$) coated titanium plate (surface area of 0.0075 m^2, 99.8% purity; Mithani (I), Ltd., India) acted as the anode with an interelectrode distance of 0.5 cm. The mixed oxide electrodes were prepared via the thermal decomposition process, as described in the literature.[28] The coating solution for the preparation of the anodes was prepared from the chlorides of the three metals, viz., $RuCl_3 \cdot x H_2O$ (38.4% ruthenium; Johnson Mathey, U.K.), $TiCl_4$ (25.1% titanium; Riedel de Haan AG, Germany), and $SnCl_4 \cdot 5H_2O$ (33.9% tin; J.T. Baker Chemical Co., USA). The salts of the aforementioned three metals were taken in the ratio of 30 RuO_2/50 TiO_2/20 SnO_2, dissolved in 2-propanol (Johnson Mathey, U.K.), and then painted over the pretreated titanium mesh (which was polished, degreased, and etched in a 10% oxalic acid (Johnson Mathey, U.K.) solution at 363 K for 30 min) to produce a uniformly spread layer. The paint layer was dried at 353 K in an air oven for 10 min to evaporate the solvent. The samples were then transferred to a muffle furnace that was maintained at 673 K for 10 min. During this period, the heating zone of the furnace was maintained with a good supply of air from a compressor. The electrode was then removed from the furnace and cooled. The process of brushing the coating solution, drying at 353 K, and then heating in the presence of air at

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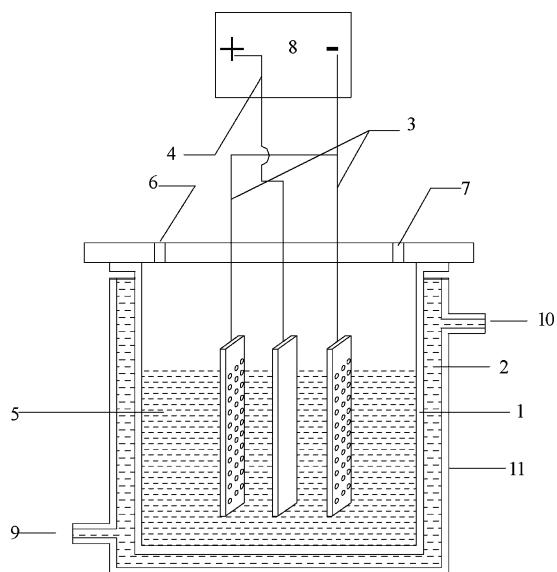
Figure 1. Schematic of the laboratory-scale cell assembly. Legend: 1, cell; 2, thermostatic water; 3, stainless steel cathode; 4, anode; 5, electrolyte; 6 & 7, holes to introduce pH sensor and thermometer; 8, dc source; 9, inlet; 10, outlet; and 11, thermostat.

Table 1. Composition of the Solid Effluent

sludge number	constituent	amount (%)
1	soluble chromium, in the form of Na_2CrO_4	1.13
2	total chromium, in the form of Cr_2O_3	13.70
3	free alkali, in the form of Na_2CO_3	1.7
4	calcium, in the form of CaO	30.75
5	magnesium, in the form of MgO	12.93
6	aluminum, in the form of Al_2O_3	14.40
7	iron, in the form of FeO	17.86
8	silica, SiO_2	5.53

673 K was repeated 6−8 times. After the final coating, the electrode was heated at 723 K for 1 h and allowed to cool in the oven itself over a period of 8 h. The cathodes were perforated stainless steel (SS 304; SAIL, India) sheets of the same size as the anode and placed on either side of the central anode at an interelectrode distance of 0.005 m. The temperature of the electrolyte was controlled to the desired value with a variation of 303 ± 2 K by adjusting the rate of flow of thermostatically controlled water through an external glass-cooling spiral. A regulated direct current was supplied from a rectifier (20 A, 15 V).

A quantity (0.45 L) of 3% sodium chloride (NaCl) was used as an electrolyte. Laboratory-grade NaCl was used for each experiment. Ten grams of the sludge was suspended in the electrolyte during the electrolysis. Current and extraction efficiencies were calculated as a function of experimental variations, such as pH, concentration of hypochlorite, particle size, pretreatment of sludge, stirring, etc. The concentration of chloride, hypochlorite, and chromate (Cr_2O_3) were all analyzed before and after extraction, using standard analytical procedures.[29] The composition of the solid effluent is shown in Table 1.

Results and Discussion

Effect of pH on the Extraction Efficiency. The electrolyte pH is an important variable in the production of hypochlorite. It is established that increasing the solution pH to 7.5 increases the current efficiency of hypochlorite. However, the hypochlorite must oxidize the Cr(III) species, which is present in a hard ceramic form, and the reaction of hypochlorite is with a solid
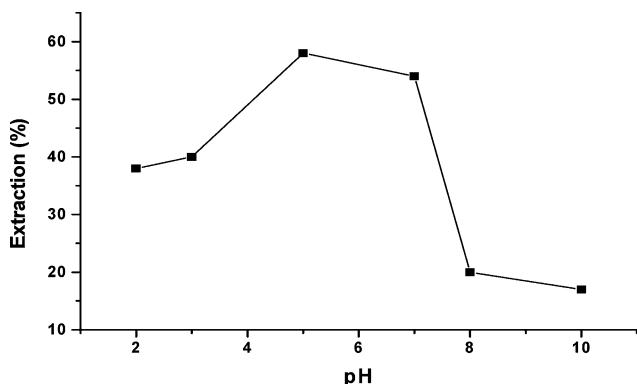
Figure 2. Effect of pH on the extraction efficiency of chromium. Conditions: electrolyte (NaCl) concentration, 30 g/L; volume, 400 mL; mass of sludge, 10 g; current density, 10 A/dm^2; duration of electrolysis, 30 min.
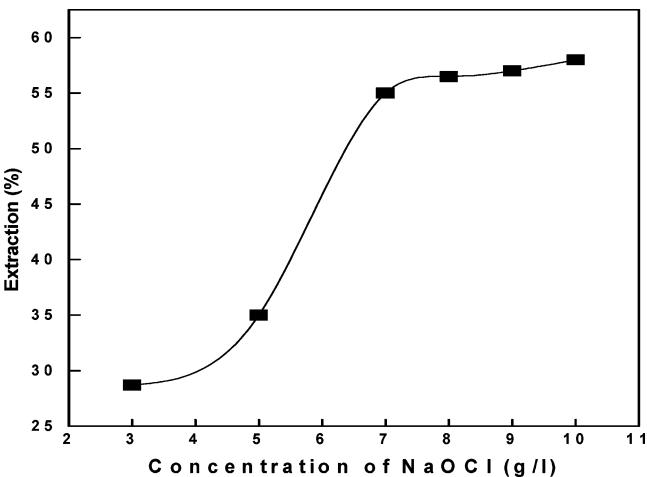
Figure 3. Effect of concentration of hypochlorite on extraction efficiency. Conditions: electrolyte (NaCl) concentration, 30 g/L; volume, 400 mL; pH, 5.0−5.5; mass of sample, 10 g; current density, 10 A/dm^2; duration of electrolysis, 30 min.

material. Therefore, the hypochlorite ion alone is not enough to break the hard solid. The presence of hypochlorous acid along with hypochlorite enhances the extraction efficiency, which will be formed at pH 5−7. Therefore, the greatest extraction was obtained between pH 5 and pH 7. Extraction efficiency was low at pH <5 and pH >7. This is due to the nonavailability of hypochlorite and hypochlorous acid, respectively. This will be evident from the data in Figure 2.

Effect of Concentration of Hypochlorite on the Extraction Efficiency. The reaction of hypochlorite with the sludge is dependent on its concentration. The solid residue does not seem to react or reacts only slowly with dilute hypochlorite solutions, even though the pH of the electrolyte is maintained at the required values. As shown in Figure 3, the use of dilute hypochlorite gives a lower percentage of extraction and the hypochlorite consumption is only ~38%. However, with a hypochlorite concentration of 7−8 g/L, the utilization of hypochlorite is >65% and also gives a higher percentage of extraction.

Effect of Particle Size of the Solid Effluent on the Extraction Efficiency. The results of these studies show a clear dependence of extraction efficiency on the particle size and are presented in Table 2. The extraction efficiency of chromium is maximum (51%) when the particle size is <50 μm. When it is <150 μm, the extraction is reduced to 46%. The same trend is noticed for the NaOCl utilization efficiency (71%−74%). This is due to the fact that, as the particle size decreases, the effective

Table 2. Effect of Particle Size of the Solid Effluent on Extraction Efficiency[a]

sludge number	particle size (μm)	total Cr$_2$O$_3$ (%)	NaOCl utilization efficiency (%)	extraction (%)
1	as received	13.70	60	45
2	<50	12.40	71	51
3	<65	13.90	56	50
4	<150	14.00	47	46

[a] Conditions: electrolyte (NaCl) concentration, 30 g/L; volume, 430 cm^3; pH, 5.0–5.5; mass of sample, 10 g; current density, 10 A/dm^2; duration of electrolysis, 10 min.

Table 3. Effect of Pretreatments on the Extraction Efficiency[a]

sludge number	constituent	amount (%)
1	as received	18.0
2	boiling in water and removing soluble chromate	32.5
3	heating with 0.1 M NaOH	20.0
4	heating with HNO$_3$ (1.25%)	3.1
5	heat with H$_2$SO$_4$ (3%)	29.0

[a] Conditions: electrolyte volume, 430 cm^3; initial pH, 2.0; final pH, 7.0; mass of sample, 10 g; current density, 10 A/dm^2; duration of electrolysis, 30 min.

Table 4. Effect of the Nature of Acid for Maintaining the pH of the Electrolyte[a]

sludge number	acid used	total Cr$_2$O$_3$ (%)	NaOCl utilization efficiency (%)	extraction (%)
1	HCl	1.60	1.56	29
2	HNO$_3$	1.63	2.00	16
3	HClO$_4$	2.00	1.72	18
4	H$_2$SO$_4$	1.56	1.50	33

[a] Conditions: electrolyte (NaCl) concentration, 30 g/L; volume, 430 cm^3; initial pH, 2.0; final pH, 7.0; mass of sludge, 10 g; current density, 10 A/dm^2; duration of electrolysis, 30 min.

Figure 4. Effect of the ratio of hypochlorite to sludge on the extraction. Conditions: electrolyte (NaCl) concentration, 30 g/L; pH, 5.0–5.5; mass of sample, 10 g; current density, 10 A/dm^2.

surface area of particles per unit volume increases and the attack of the hypochlorite on the particle is more efficient.

Effect of Pretreatment of Sludge on the Extraction Efficiency. For pretreatment of the sludge, powdered solid residue (100 g) was placed with 0.5 L of water in a 1.0-L beaker. The contents of the beaker was heated to boiling and maintained at boiling temperature for ~15 min. After cooling, the contents were filtered through a Whatman (No. 42) filter paper, the residue was dried at 383 K for 1 h, and 10 g of sample was used for an electrochemical extraction. The aforementioned procedure was followed for NaOH (0.1 M), HNO$_3$ (1.25%), and H$_2$SO$_4$ (3%).

The effect of pretreatment of the sludge with various reagents on the extraction efficiency of chromium is presented in Table 3. The table indicates that the efficiency of extraction is greater with water-treated samples than that for as-received samples. This may be because the alkali content of the residue decreases after water washing and helps to maintain the pH in the acidic region. This will be evident from the higher extraction after treatment with sulfuric acid. Treatment with nitric acid actually decreases the efficiency, probably because the presence of the nitrate ion reduces the hypochlorite formation. Alkaline treatment with NaOH must help to bring some of the constituents into solution. However, hypochlorite is present totally as ClO$^-$, the oxidation ability of which is low at pH >7.0. Thus, the removal of soluble chromate by washing with water before initiating the extraction leads to a much higher extraction percentage and helps to maintain a favorable pH during extraction.

Effect of the Choice of the Acid for pH Maintenance on the Extraction Efficiency. The oxidation of acid is required to maintain the favorable pH for the maximum extraction percentage. To reduce the build up of chloride ions in the electrolyte and to explore the possibility of enhancing the reaction efficiency via the addition of other anions, different acids were used to maintain the pH at the desired pH. The results in Table 4 indicate that the use of hydrochloric acid (HCl) gives a lower concentration of untreated hypochlorite and also gives an appreciable extraction percentage, when compared with the use of nitric and perchloric acids. However, the use of sulfuric acid also gives an appreciable extraction percentage; but, the

increase in sulfate concentration will result in oxygen evolution at the anode, thus reducing the anode life, and the removal of sodium sulfate also is difficult after extraction. From the point of view of working out a cyclic process with respect to the utilization of chloride, it was deemed appropriate to use for pH maintenance.

Effect of the Ratio of Hypochlorite to Sludge on the Extraction. The reaction of the solid effluent with the hypochlorite under optimum conditions of pH, concentration of hypochlorite, etc., is expected to occur as per eq 1:

$$3Cr_2O_3 + 3HOCl + 6NaOCl + 3H_2O \rightarrow$$
$$3Na_2Cr_2O_7 + 9H^+ + 9Cl^- \quad (1)$$
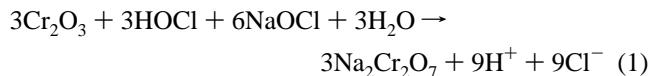
Because the rate of the reaction is dependent on the mutual concentration of the reactions, experiments were conducted at different ratios of hypochlorite to the sludge, keeping the other parameters constant. The results of the study are shown in Figure 4. The figure shows that the extraction efficiency is at a maximum when the ratio of Cr(III) to NaOCl is 1:2. When the sludge concentration is greater, the extraction of the chromium is low and the unreacted sludge contained more recoverable Cr(III). If the hypochlorite content is high, the balance of the hypochlorite after reaction with the sludge gets converted to chlorate, because of the stirring and pH. It will be concluded that when the ratio of Cr(III) to NaOCl is 1:2, the extraction efficiency is at a maximum.

Effect of Stirring on the Extraction Efficiency. The formation of hypochlorite increases as the rate of hydrolysis of the chlorine, which is evolved at the anode, increases. From dilute chloride solutions, its mass transfer from the bulk to the anodic surface limits the evolution of chlorine and stirring the electrolyte improves the rate of transfer of chloride to the anode. This again increases the hydrolysis and formation of hypochlorite. Moreover, the stirring also improves the rate of
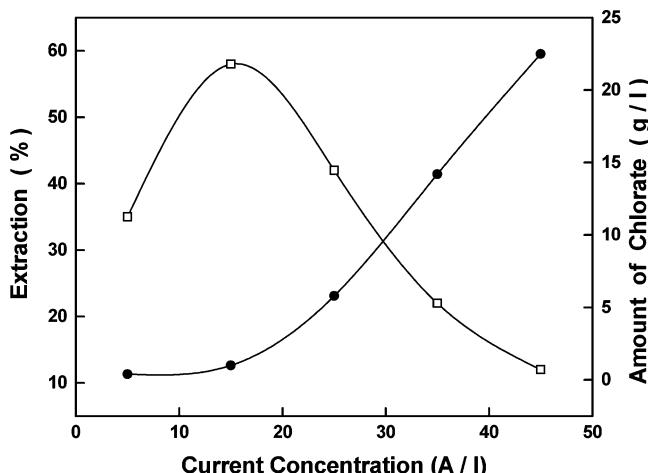
Figure 5. Effect of current concentration on extraction efficiency. Conditions: electrolyte (NaCl) concentration, 30 g/L; pH, 5.0−5.5; mass of sample, 10 g; current density, 10 A/dm^2.

reaction of the suspended sludge particles with the hypochlorite and the utilization efficiency of the hypochlorite also improves. The stirring rate was also determined to attain a critical value, ~0.3 m/S, beyond which there was no improvement in the extraction. And above this rate of stirring, it was adversely affected by the reaction, because of the increase in the concentration of chlorate because of the chemical reaction of HClO and ClO$^-$. Stirring also helps to maintain the pH of the electrolyte and a uniform distribution of the acid added to keep the pH at the desired level.

Effect of Current Concentration on the Extraction Efficiency. Current concentration is the quantity of electricity applied per unit volume of the electrolyte, and this parameter is expressed in terms of amperes per liter (A/L). During electrolysis, for a fixed quantity of current, the current concentration increases as the volume decreases. As the volume decreases, the effective concentration of hypochlorite per liter increases, although the total quantity of hypochlorite formed will be the same, assuming that the current efficiency is constant.

To facilitate the handling of a large volume of electrolyte in the large scale and expecting an increase in the rate of the extraction as the effective concentration of the hypochlorite is increased, experiments were conducted at various current concentrations. Figure 5 shows that the current efficiency for the formation of hypochlorite decreases as the current concentration increases. The Cr(III) extraction reaches a maximum at a current concentration of 10−15 A/L; beyond this range of values, the extraction decreases. The reason for the decrease in both with high current concentration can be understood from the increase in the chlorate concentration from 0.4 g/L to 22.5 g/L. In view of this, the optimum current concentration lies in the range of 10−15 A/L.

Conclusion

The study on the extraction of Cr(III) from solid effluent from a chromate plant leads to the following conclusions:

(1) Electrochemical hypochlorite generation at a concentration of ~7 g/L in a batch-type cell is obtained at a maximum efficiency of 45%−55% with a metal-oxide-coated titanium anode and a stainless steel cathode at a current density of 10−15 A/dm^2 at a sodium chloride (NaCl) concentration of 30−40 g/L in a solution that has been maintained at a temperature of 203 K.

(2) The oxidation and extraction of Cr(III) in the chromate plant sludge with in-situ-generated hypochlorite are at maximum efficiency under the following conditions: (i) the particle size of the sludge must be below a range of 50−150 μm; (ii) a ratio of Cr(III) to NaOCl in the range of 1:1.8 to 1:2 results in better recovery of the Cr(III) species; (iii) a pH of 2−6 during the electrolysis gives a high extraction percentage; (iv) a current concentration of 11−12 A/L is needed for maximum extraction; and (v) agitation at a rate of 0.3 m/S produces an effective reaction rate.

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