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CENTRE DES TECHNOLOGIES DE L'EAU

Chromium recovery from electroplating rinsing waters using a novel metal exchange technology

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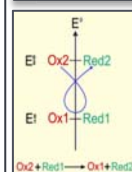
Objectives

Development of a new technology for chromium recovery from surface finishing industries' wastewaters. This technology is based on the utilization of zero valent iron fibers as an exchange and electron donor media for reducing chromium from its toxic hexavalent form to its less toxic three valent form, followed by precipitation as chromium hydroxide.

Metal exchange process

Exchange of a less electronegative metal with another more electronegative metal

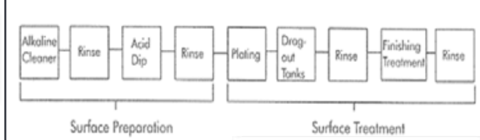


$E_1^0 < E_2^0$

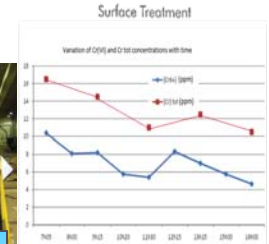
Reduction (acceptors)	E° (V)	Oxidation (donnors)	E° (V)
$Cr_2O_7^{2-} + 14H^+ + 6e^- \leftrightarrow 2Cr^{3+} + 7H_2O$	+1,33	$Fe(s) \leftrightarrow Fe^{2+}(aq) + 2e^-$	+0.44
$HCrO_4^- + 7H^+ + 3e^- \leftrightarrow Cr^{3+} + 4H_2O$	+1,20		

$$HCrO_4^-(aq) + 7H^+(aq) + Fe^0(s) \rightarrow Cr^{3+}(aq) + Fe^{3+}(aq) + 4H_2O(l)$$

Chromium sources: rinsing waters



Rinsing water steps in an electroplating process



Typical chromium concentrations profile

Results

pH initial =3. Flow rate 10 ml/min.
Contact time 16.6 min.

Time (min)	pH	Conductivity (µS/cm)	$[Cr^{6+}]$ (ppm)	[Cr total] (ppm)	Total chromium removal (%)
Before treatment	3,03	225	16	20	-
0,6	6,24	1815	0,15	0,44	97,8
1	6,69	1540	0,2	0,26	98,7
2	6,78	1197	0,2	0,21	98,9
3	6,85	887	0,12	0,17	99,1
5	6,86	543	<DL	<DL	100
10	6,72	283	<DL	<DL	100
15	6.70	220	<DL	<DL	100

$$2Fe^0_{(s)} + O_{2\,(g)} + 2H_2O_{(l)} \rightarrow 2Fe^{2+}_{(aq)} + 4HO^-_{(aq)}$$

$$Fe^0_{(s)} + 2H_2O_{(l)} \rightarrow Fe^{2+}_{(aq)} + H_{2\,(g)} + 2HO^-_{(aq)}$$

Mechanism of pH increase

- Significant increase of pH
- Cr(VI) is completely reduced to Cr(III)
- Cr(III) precipitates inside the column
- Conductivity increases at the beginning and then decreases due to formation of Fe(II) ions which are oxidized to Fe(III) and precipitates as feric hydroxide
- 100% removal of total chromium

Two industrial scale installations

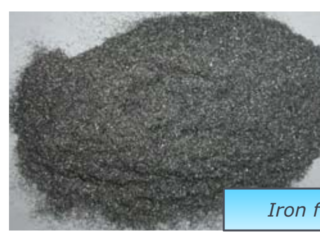
Rinsing water quality control unit system

Iron fiber after saturation (inside the column)

Patent # 20140353258

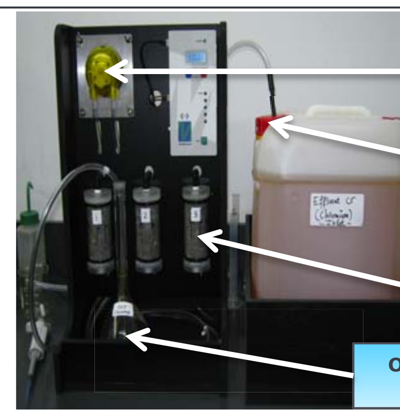
Methodology

(lab-scale tests)



Iron fiber

Compacted Mixture of iron and cellulose fibers (pressure)



Wastewater volume (liters)	Inlet of column			Outlet of column		
	pH	[Cr(VI)] (ppm)	[Cr(total)] (ppm)	pH	[Cr(VI)] (ppm)	[Cr(total)] (ppm)
156	3.5	10.4	18.5	5.0	<0.01	<0.02
456	3.4	6	12	5.2	<0.01	<0.02
896	3.5	7	14.3	5.2	<0.01	<0.02
1520	3.6	9.2	21	5.3	<0.01	<0.02
2240	3.4	7.8	18	5.3	<0.01	<0.02
3300	3.5	5.6	14	5.6	<0.01	<0.02
4560	3.5	8.6	20.5	5.4	<0.01	<0.02
6500	3.4	7.8	17	5.0	<0.01	<0.02
7100	3.2	8.8	20.3	5.2	<0.01	<0.02
8890	3.6	8	16	5.4	<0.01	<0.02
11250	3.4	12	15.2	5.3	<0.01	<0.02
13500	3.4	7	13.6	5.0	<0.01	<0.02
15600	3.5	8.3	14	4.8	<0.01	<0.02
17620	3.5	8.6	18	4.8	<0.01	<0.02
22000	3.3	9	19.9	4.8	<0.01	<0.02
23540	3.2	11	23	5.0	<0.01	<0.02
25600	3.8	7.3	15	5.1	<0.01	<0.02
26650	3.5	7.9	18	5.3	<0.01	<0.02
28360	3.6	8.3	19	5.4	<0.01	<0.02
30300	3.3	5	11	5.2	<0.01	<0.02
32000	3.4	9	20	4.8	<0.01	0.022
34500	3.5	12	26	4.9	<0.01	0.11
36780	3.7	11.6	22	5.2	<0.01	0.21
39450	3.8	15	23	5.0	<0.01	<0.02
40200	3.5	16	25	5.3	<0.01	<0.02
43600	3.4	8	18	5.2	<0.01	<0.02
46694	3.5	6.3	11.6	5.4	<0.01	0.22
48600	3.6	7.9	18	5.3	<0.01	0.2
51200	3.7	8.6	17	5.0	<0.01	0.8
55000	3.3	8.6	19	4.8	<0.01	<0.02
57600	3.7	9	22	4.8	<0.01	0.065
60200	3.5	8.8	19.6	4.8	<0.01	<0.02
64300	3.5	9.3	22	5.0	<0.01	<0.02
66540	3.5	5.6	12	5.1	<0.01	0.11
68900	3.5	4.3	9	5.3	<0.01	0.44
71360	3.7	11.6	22	5.4	<0.01	0.6
75000	3.8	7	15	5.2	<0.01	0.45
78600	3.5	8.2	18	4.8	<0.01	0.2
80210	3.5	8	16	4.9	<0.01	0.03
83500	3.5	8.9	20	5.2	<0.01	0.32
85000	3.6	11.3	23	5.0	<0.01	0.44

Conclusions

- New metal exchange technology, very efficient and compact
- No addition of harmful and dangerous chemicals
- Chromium recovery yield almost 100%
- Recovery of chromium as a recyclable residue
- No sludge production
- Cost-effective technology
- Complies to most local environmental regulations
- Considerable rinsing water savings
- Continuous rinsing water quality control
- Patented technology

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