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(54) A METHOD FOR ELECTROWINNING OF METALLIC CHROMIUM FROM ACIDIC WASTE ELECTROLYTES

(57) The invention consists in an acidic electrolyte solution with a Cr(VI) ion concentration of more than 0.05 g/l being subjected to electrolysis using an anode made of steel or lead and a cathode made of steel, graphite or glassy carbon that is at least 10 times smaller than the anode, wherein the electrolysis is carried out potentiostatically or galvanostatically.

For the lead anode, the cathode potential remains within the range from -2.9 V to -3.5 V and for the steel anode, the cathode potential remains within the range from -2.5 V to -3.0 V. The cathodic current density remains constant within the range from 0.06 A/cm^2 to 0.7 A/cm^2 in acidic solutions containing more than 50 g/l of chromium. Alternatively, the electrolysis is carried out using controlled current pulse, wherein the cathodic current density remains constant within the range from 0.06 A/cm^2 to 0.7 A/cm^2 in acidic solutions containing more than 50 g/l of chromium, and the pulse off-time is from 10 to 20% of the electrolysis duration, which is over 10 s.

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Description

[0001] The subject of the invention is a method for electrowinning of metallic chromium from aqueous acidic waste solutions of complex composition.

[0002] Due to environmental concerns, in recent years most countries of the world have been changing rules and tightening requirements for all human activities in the scope of water, soil and air protection. At the same time, in the era of expansive human economy, the demand for metals, including heavy metals, has increased to such an extent that some of these resources are running out. A growing concern is also the deteriorating quality of ores mined worldwide, the decline in the quality of concentrates and metal yields, as well as the rising cost of metal production.

[0003] This situation makes it necessary to endeavour to increasingly recover raw materials, including chromium compounds from waste solutions.

[0004] Dangerous sewage containing highly toxic chromium originates mainly from tanneries, dyeworks, electroplating plants, chromium plants etc. Despite many studies on chromium recycling, the problem of its recovery, especially in metallic form, along with the simultaneous sewage treatment, remains unresolved. The technology of disposal of waste containing Cr(VI) uses almost exclusively a reduction method of Cr(VI) chromium ions to Cr(III), involving the precipitation of insoluble chromium hydroxide, which is then stored at a solid waste landfill.

[0005] The patent application P. 381 326 discloses a method for comprehensive management of tannery waste, including chromium solid waste, combined with processing of sewage sludge, including sludge containing chromium (III). This method consists in the purification of waste and sludge from chromium during the initial stages of the closed process, both by leaching chromium (III) with working solutions containing at least one base salt, one extractant and one pH regulator, and by liquid/liquid extraction removal using a catalyst of phase transfer of chromium (III) and other, previously complexed, trivalent metals from waste water into the organic phase. Purified waste and sludge and inorganic compounds generated in the course of their treatment are processed into valuable products during subsequent process stages. The method results in recovering untanned hide collagen with intact fibrous structure, chromium compounds and other inorganic salts which were previously pollutants of chromium sewage sludge.

[0006] U.S. patent US4948476 discloses a method for recovering chromium from industrial sludge and a device for applying the method. Electrolysis of the solution containing chromium ions is carried out in a system composed of at least one anode, one cathode and an anion exchange membrane which are connected to a DC power source. The membrane is made of poly(p-trimethylaminomethyl)styrene, poly(p-dimethylaminomethyl)styrene or (tetramethylammonium)ethylene. The separation of Cr(III), present in the waste together with other metals/components, takes place during the electrolysis. The separation consists in that at the first stage Cr(III) on the anode is oxidized (at least partially) to soluble Cr(VI) compounds, and subsequently a selective membrane is used through which the Cr(VI) ions (anions) thus obtained are transmitted to another part of the electrolysis cell, where chromium in the form of Cr(VI) anion is collected, e.g. by way of precipitation of insoluble salts.

[0007] The essence of the invention is that the acidic electrolyte solution with a Cr(VI) ion concentration of more than 0.05 g/l is subjected to electrolysis using an anode made of steel or lead and a cathode made of steel, graphite or glassy carbon that is at least 10 times smaller than the anode, wherein the electrolysis is carried out potentiostatically or galvanostatically. For the lead anode, the cathode potential remains within the range from -2.9 V to -3.5 V and for the steel anode, the cathode potential remains within the range from -2.5 V to -3.0 V. The cathodic current density remains constant within the range from 0.06 A/cm^2 to 0.7 A/cm^2 in acidic solutions containing more than 50 g/l of chromium. Alternatively, the electrolysis is carried out using controlled pulsed current, wherein the cathodic current density remains constant within the range from 0.06 A/cm^2 to 0.7 A/cm^2 in acidic solutions containing more than 50 g/l of chromium, and the pulse off-time is from 10 to 20% of the electrolysis duration, which is over 10 s.

[0008] Preferably, metallic chromium precipitates on the cathode in the form of flakes, powder or nanopowder.

[0009] Preferably, the electrolysis duration depends on the initial and final chromium content in the electrolyte, on the electrolyte volume, and on whether the metallic chromium obtained is supposed to be in the form of flakes, powder or nanopowder.

[0010] The main advantage of the above-presented invention is that it does not involve a very expensive stage of chemical reduction of Cr(VI) to Cr(III) ions, and the product obtained as a result of the method is metallic chromium, not its compound. Thus, the cost of the application of the solution in question is lower, and the product obtained, namely metallic chromium, is much more valuable than chromium salts, oxides or hydroxides obtained with prior art technology. It is particularly advantageous to use this invention for the selective waste electrolysis, since it enables the production of chromium in the form of flakes, powders and nanopowders with purity over 99.7%.

[0011] The invention is now described in more details by references to the following examples.

Example I

[0012] In an electrochemical vessel thermostatted to 25°C there is a lead anode with an area of approx. 100 cm^2 which is also a reference electrode in a two-electrode system and the cathode is a graphite rod with an area of approx. 0.6 cm^2. The vessel is filled with electrolyte mainly composed of the following: 109.6 g/l Cr (mainly Cr(VI)), 10 g/l H_2SO_4 and 20.6 mg/l Cu.

[0013] The electrolysis is carried out potentiostatically with a potential of -3.5 V and an average current density of 0.385 A/cm^2 over 30 minutes.

Example II

[0014] In an electrochemical vessel thermostatted to 25°C there is a lead anode with an area of approx. 100 cm^2 which is also a reference electrode in a two-electrode system and the cathode is a copper plate with an area of approx. 2.4 cm^2. The vessel is filled with electrolyte mainly composed of the following: 109.6 g/l Cr (mainly Cr(VI)), 10 g/l H_2SO_4 and 20.6 mg/l Cu.

[0015] The electrolysis is carried out galvanostatically with a potential of -3.40 V and current density of 0.208 A/cm^2 over 120 minutes.

Example III

[0016] In an electrochemical vessel thermostatted to 25°C there is a lead anode with an area of approx. 100 cm^2 which is also a reference electrode in a two-electrode system and the cathode is a steel plate with an area of approx. 2.2 cm^2. The vessel is filled with electrolyte mainly composed of the following: 109.6 g/l Cr (mainly Cr(VI)), 10 g/l H_2SO_4 and 20.6 mg/l Cu.

[0017] The electrolysis is carried out galvanostatically with a potential of -3.28 V and current density of 0.227 A/cm^2 over 120 minutes.

Example IV

[0018] In an electrochemical vessel thermostatted to 25°C there is a lead anode with an area of approx. 100 cm^2 which is also a reference electrode in a two-electrode system and the cathode is a steel plate with an area of approx. 2 cm^2. The vessel is filled with electrolyte mainly composed of the following: 109.6 g/l Cr (mainly Cr(VI)), 10 g/l H_2SO_4 and 20.6 mg/l Cu.

[0019] The electrolysis is carried out using controlled pulsed current over the period of 3.5 hours with a 30 min break. Current density is 0.2 A/cm^2.

Claims

1. A method for electrowinning of metallic chromium from acidic waste electrolytes **wherein** the acidic electrolyte solution with a Cr(VI) ion concentration of more than 0.05 g/l is subjected to electrolysis using an anode made of steel or lead and a cathode made of steel, graphite or glassy carbon that is at least 10 times smaller than the anode, wherein the electrolysis is carried out potentiostatically or galvanostatically, with the cathode potential for the lead anode remaining within the range from -2.9 V to -3.5 V and with the cathode potential for the steel anode remaining within the range from -2.5 V to -3.0 V, while the cathodic current density remains constant within the range from 0.06 A/cm^2 to 0.7 A/cm^2 in acidic solutions containing more than 50 g/l of chromium, or using controlled pulsed current, wherein the cathodic current density remains constant within the range from 0.06 A/cm^2 to 0.7 A/cm^2 in acidic solutions containing more than 50 g/l of chromium, and the pulse off-time is from 10 to 20% of the electrolysis duration, which is over 10 s.

2. A method according to claim 1 **wherein** the metallic chromium precipitates on the cathode in the form of flakes, powder or nanopowder.

3. A method according to claim 1 **wherein** the electrolysis duration depends on the initial and final chromium content in the electrolyte, on the electrolyte volume, and on whether the metallic chromium obtained is supposed to be in the form of powder, flakes or nanopowder.

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EUROPEAN SEARCH REPORT

Application Number
EP 15 46 0013

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	DE 639 446 C (IG FARBENINDUSTRIE AG) 5 December 1936 (1936-12-05)	1-3	INV. C25C1/10 C25C5/02
Y	* claims 1-6; example 1 * -----	1	
Y	US 5 433 797 A (ERB UWE [CA] ET AL) 18 July 1995 (1995-07-18) * column 3, lines 48-55; claims 1,2 * -----	1	
A	US 1 544 451 A (CARL HAMBUECHEN) 30 June 1925 (1925-06-30) * claims 1-8 * -----	1-3	
A	US 2 803 594 A (WESTBY GEORGE C) 20 August 1957 (1957-08-20) * column 2, line 72 - column 3, line 53 * -----	1-3	
			TECHNICAL FIELDS SEARCHED (IPC)
			C25C

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	9 October 2015	Hammerstein, G

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 15 46 0013

09-10-2015

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
DE 639446	C	05-12-1936	NONE	
US 5433797	A	18-07-1995	NONE	
US 1544451	A	30-06-1925	NONE	
US 2803594	A	20-08-1957	NONE	

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- WO P381326 A **[0005]**
- US 4948476 A **[0006]**