

IRON CHROMIUM ELECTROLYTES

5 THIS INVENTION relates to iron chromium electrolytes. In particular, the invention relates to a process for producing an iron chromium electrolyte or a raw iron chromium electrolyte, to a raw iron chromium electrolyte and a purified iron chromium electrolyte produced by a process in accordance with the invention, to use of a purified iron chromium electrolyte produced by a process in accordance with the invention in an iron chromium redox flow battery, and to an iron chromium redox flow battery which includes a purified iron chromium electrolyte produced by a process in accordance with the invention.

 Iron chromium redox flow batteries (ICRFB's) are known, having been studied extensively during the 1970's and 1980's. Energy is stored and released by using the Fe^{2+} - Fe^{3+} and Cr^{2+} - Cr^{3+} redox couples, with the iron and chromium species being fully dissolved in an aqueous iron chromium electrolyte at all times. It stands to reason that, at least for use in ICRFB's, there is a need for an efficient, safe, low cost process to produce iron chromium electrolytes, and for iron chromium electrolytes produced by such a process.

20 According to one aspect of the invention, there is provided a process for producing an iron chromium electrolyte, the process including

 leaching iron and chromium from a ferrochrome alloy at an elevated leaching temperature, using hydrochloric acid, to produce a raw iron chromium electrolyte comprising dissolved iron and dissolved chromium; and

25 purifying the raw electrolyte to produce a purified iron chromium electrolyte.

 The term "purified iron chromium electrolyte" in this specification is not limited to but includes within its meaning a "functional iron chromium electrolyte", meaning an electrolyte that is functionally suitable as an iron chromium electrolyte of an iron chromium redox flow battery. The purified iron chromium electrolyte herein described is such a functional iron chromium electrolyte.

In this regard, purification may include adjustment of Fe content, Cr content, and/or of electrical conductivity, as herein described, to produce such a functional iron chromium electrolyte.

5 According to another aspect of the invention, there is provided a process for producing a raw iron chromium electrolyte, the process including

 leaching iron and chromium from a ferrochrome alloy at an elevated leaching temperature, using hydrochloric acid, to produce said raw iron chromium electrolyte comprising dissolved iron and dissolved chromium.

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 The ferrochrome alloy may have an Fe content of between about 35% by mass and about 45% by mass, preferably between about 37% by mass and about 44% by mass, more preferably between about 39% by mass and about 44% by mass, e.g., about 42% by mass.

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 The ferrochrome alloy may have a Cr content of between about 45% by mass and about 60% by mass, preferably between about 46% by mass and about 54% by mass, more preferably between about 48% by mass and about 52% by mass, e.g., about 50% by mass.

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 The ferrochrome alloy may be particulate ferrochrome alloy, e.g. milled or atomised ferrochrome alloy.

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 The particulate ferrochrome alloy may have a particle size with a D50 of between about 0.5mm and about 1.5mm, preferably between about 0.5mm and about 1.2mm, more preferably between about 0.5mm and about 1mm.

 The hydrochloric acid may be at a molar concentration of between about 3M and about 8M, preferably about 6.0M.

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 A ratio of ferrochrome alloy to hydrochloric acid (weight per volume) may be in the range of about 100g/ℓ to about 200g/ℓ, preferably in the range of about 120g/ℓ to about 180g/ℓ, more preferably in the range of about 140g/ℓ to about 170g/ℓ, e.g., about 155g/ℓ.

The elevated leaching temperature may be between about 80°C and about 100°C, preferably between about 85°C and about 95°C, more preferably between about 95°C and about 100°C, e.g., about 95°C.

5 The iron and chromium may be leached from the ferrochrome alloy for a period of between about 30 minutes and about 24 hours, preferably between about 8 hours and about 14 hours, more preferably between about 4 hours and about 12 hours, e.g., for a period of about 14 hours. This period may be the actual leach time used in a process in accordance with the invention employing a batch leaching step, or the average total leach residence time of solids
10 material in a leaching stage of a process in accordance with the invention which employs a continuous leaching stage.

 The iron and chromium may be leached from the ferrochrome alloy in a solid-liquid fluidised bed. Preferably, maximum chromium and iron are leached from the ferrochrome
15 alloy and dissolved in the hydrochloric acid.

 During the leaching of the ferrochrome alloy, hydrogen would typically be produced. The process thus typically includes removing hydrogen from a leaching vessel, e.g., a solid liquid fluidised bed leaching vessel used in a leaching step during which the leaching is
20 effected. The hydrogen removed from the leaching vessel may be flared, or may be captured for future use.

 During the leaching of the ferrochrome alloy, a solids residue is typically produced, in addition to the raw iron chromium electrolyte and the hydrogen. The process thus typically
25 includes separating the raw iron chromium electrolyte from the solids residue, e.g., by filtration, before the raw iron chromium electrolyte, e.g., in the form of a filtrate, is purified. The solids residue is typically returned to a smelting process.

 Purifying the raw iron chromium electrolyte may include removing unwanted
30 metallic and/or non-metallic impurities from the raw iron chromium electrolyte.

 In some cases, the ferrochrome alloy may have, as an unwanted metallic content, a low titanium content, e.g., about 0.1% by mass to about 0.3% by mass titanium. As will be

appreciated, during the leaching of a ferrochrome alloy that includes titanium with hydrochloric acid, TiCl_4 is formed. Purifying the raw iron chromium electrolyte may then include removing titanium from the raw iron chromium electrolyte.

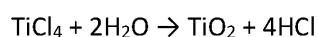
5 Removing titanium from the raw iron chromium electrolyte may include subjecting the raw iron chromium electrolyte to a crystallisation step to form a slurry of FeCl_2 crystals, CrCl_3 crystals and TiO_2 crystals. The crystallisation step may be in the form of an evaporative cooling crystallisation step.

10 The crystallisation step may thus include heating the raw iron chromium electrolyte to an evaporation temperature of at least about 90°C , preferably at least about 95°C , more preferably to boiling temperature. Typically, the raw iron chromium electrolyte boils at a temperature in the range of about 90°C to about 95°C .

15 The crystallisation step may include maintaining the raw iron chromium electrolyte at the evaporation temperature, e.g., boiling temperature, until first solid crystals are observed.

20 As will be appreciated, during the heating of the raw iron chromium electrolyte to the evaporation temperature, and while the raw iron chromium electrolyte is maintained at the evaporation temperature, water and hydrochloric acid are removed from the raw iron chromium electrolyte. The process may include recycling the water and hydrochloric acid, e.g., to leach the ferrochrome alloy.

25 At the evaporation temperature, TiCl_4 may react with water to form titanium oxide in accordance with the following reaction:



30 The crystallisation step may include cooling the raw iron chromium electrolyte to form said slurry of FeCl_2 crystals, CrCl_3 crystals and TiO_2 crystals. Typically, these crystals are small (e.g., less than 5mm).

The raw iron chromium electrolyte may be cooled to a temperature below about 50°C, preferably below about 40°C, more preferably below about 35°C, e.g., about 25°C - 30°C. Typically, the raw electrolyte is cooled to a temperature which does not go below about ambient temperature.

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The TiO_2 thus crystallises with the FeCl_2 and CrCl_3 to form said slurry of FeCl_2 crystals, CrCl_3 crystals and TiO_2 crystals. Typically, both the FeCl_2 and CrCl_3 crystals are in hydrated form, being for example in the form of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ respectively.

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Removing titanium from the raw iron chromium electrolyte may include heating the slurry of FeCl_2 crystals, CrCl_3 crystals and TiO_2 crystals to redissolve the FeCl_2 crystals and the CrCl_3 crystals, thereby forming a reconstituted electrolyte solution. The slurry may be heated to a temperature of at least about 80°C, preferably at least about 85°C, more preferably at least about 88°C, e.g., about 90°C. Typically, the slurry is heated to a temperature which does not exceed about 95°C.

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Advantageously, during heating of the slurry of FeCl_2 crystals, CrCl_3 crystals and TiO_2 crystals, the reaction of TiCl_4 with water to form TiO_2 is promoted by the higher temperature so that the TiCl_4 reacts substantially to completion. Also advantageously, the TiO_2 crystals do not dissolve, or only sparingly dissolve, with the FeCl_2 crystals and the CrCl_3 crystals, at the temperature to which the slurry of FeCl_2 crystals, CrCl_3 crystals and TiO_2 crystals is heated.

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Typically, after the heating of the slurry of FeCl_2 crystals, CrCl_3 crystals and TiO_2 crystals, the reconstituted electrolyte solution is cooled again, producing a slurry of fine TiO_2 solids (crystals) and reconstituted electrolyte solution. Typically, the fine TiO_2 crystals have a D50 of less than about 1 μm .

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The reconstituted electrolyte solution may be cooled to a temperature below about 50°C, preferably below about 40°C, more preferably below about 30°C, e.g., about 25°C. Typically, the reconstituted electrolyte solution is cooled to a temperature which does not go below about ambient temperature.

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During the crystallisation step hereinbefore described, water and excess hydrochloric acid are typically removed from the raw iron chromium electrolyte, as also hereinbefore described. The process may include adding water to the reconstituted electrolyte solution. As will be appreciated, adding water to the reconstituted electrolyte solution increases the pH of the reconstituted electrolyte solution. The increased pH advantageously assists in the precipitation of TiO_2 .

The process may include a pH adjustment step, which is performed on the raw iron chromium electrolyte or, when the process includes a titanium removal step as described above, on the reconstituted electrolyte solution. Thus, the process may include, in the pH adjustment step, adjusting the pH of the raw iron chromium electrolyte or of the reconstituted electrolyte solution, as the case may be. The pH adjustment step may form part of the purification of the raw iron chromium electrolyte or of the reconstituted electrolyte solution, as the case may be.

Preferably, the pH adjustment step is performed in conjunction with, and ahead of, an ion exchange step as hereinafter described. Such an ion exchange step may also form part of the purification of the raw iron chromium electrolyte or of the reconstituted electrolyte solution, as the case may be.

The pH adjustment step may comprise adjusting the pH to between 0.0 and 2, e.g. about 1.5. Typically, the pH is not adjusted to above about 2. Advantageously, keeping the pH below about 2 ensures that Fe^{2+} in the reconstituted electrolyte solution does not oxidise.

Adjustment of the pH may be performed by using a base, or by adding an acid. A suitable base may be sodium hydroxide, potassium hydroxide, chromium hydroxide and/or ammonium hydroxide. A suitable acid may be hydrochloric acid and/or sulphuric acid.

Removing solid impurities, such as titanium, from the raw iron chromium electrolyte may include separating solids, such as TiO_2 , from the raw iron chromium electrolyte or, when applicable, from the reconstituted electrolyte solution.

Solids separation may be effected by means of filtration.

5 Ferrochrome alloy typically includes small amounts of Ni and Cu. Purifying the raw iron chromium electrolyte may include removing Ni and Cu, which removal may be performed on the raw iron chromium electrolyte or on the reconstituted electrolyte solution if applicable, providing said purified iron chromium electrolyte.

10 Removing Ni and Cu may include contacting the raw iron chromium electrolyte or the reconstituted electrolyte solution, as the case may be, with a strong cation ion exchange resin. Examples of a suitable strong cation ion exchange resin include Puromet™ MTS9600, Felite™ FS400, and Puromet™ 9300. The removal of Ni and Cu may performed either simultaneously or separately by contacting the raw electrolyte solution with a strong cation ion exchange resin.

15 As will be appreciated, removing solids such as the TiO₂ crystals referenced above and any other solids from the raw iron chromium electrolyte or from the reconstituted electrolyte solution, as the case may be depending on which of these is subjected to ion exchange, e.g., by means of filtration, advantageously ensures that undissolved solids do not adhere to, or blind pores of, the strong cation ion exchange resin.

20 Advantageously, the strong cation ion exchange resin may be regenerated using a suitable acid, a suitable base, or water. Examples of a suitable acid that can be used for regeneration include hydrochloric acid and sulphuric acid. Examples of a suitable base that can be used include ammonium hydroxide and sodium hydroxide.

25 The process may include concentrating or diluting the purified iron chromium electrolyte.

30 Concentrating the purified iron chromium electrolyte may include heating the purified iron chromium electrolyte to evaporate water, or concentration of the purified iron chromium electrolyte using an iron and/or chromium rejecting membraned process, i.e. a process setup comprising one or more membrane separation stages, e.g. reverse osmosis or nanofiltration.

The purified iron chromium electrolyte may be heated to a temperature of at least about 85°C, preferably at least about 90°C, more preferably at least about 95°C, e.g., about 95°C. Typically, the purified iron chromium electrolyte is heated to a temperature which does not exceed the normal boiling temperature of the purified iron chromium electrolyte.

5 Advantageously, boiling can be used to quicken the concentration of the iron chromium electrolyte.

When using a membraned process is used for concentration, the purified iron chromium electrolyte may be circulated through the membraned process at a pressure of between 1 to 41 bar, preferably for example at 41 bar for nanofiltration where water is allowed to permeate the membrane while iron and chromium is retained. The purified iron chromium electrolyte may be circulated through the membrane setup at a pressure of between 1 to 80 bar, preferably for example at 80 bar for reverse osmosis where water is allowed to permeate the membrane while iron and chromium is retained. A suitable iron and chromium rejecting membrane, such a suitable membrane may be, e.g a Polyamide thin film nano filtration membrane or reverse osmosis membrane.

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The purified iron chromium electrolyte may be concentrated or diluted to a Cr and/or Fe concentration of at least about 80g/ℓ, preferably at least about 75g/ℓ, more preferably at least about 72g/ℓ, e.g., about 72g/ℓ. Typically, the purified iron chromium electrolyte is not concentrated beyond a Cr concentration of about 86g/ℓ.

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The process may include adjusting the Fe and/or Cr concentration of the purified iron chromium electrolyte upwards.

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Adjusting the Fe concentration of the purified iron chromium electrolyte upwards may include adding Fe as metal, or Fe as a salt such as iron sulphate or iron chloride.

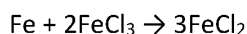
Adjusting the Cr concentration of the purified iron chromium electrolyte upwards may include adding Cr as metal, or as a Cr salt such as chromium sulphate or chromium as chromium chloride.

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The Fe and/or Cr concentration of the purified iron chromium electrolyte may be adjusted to an Fe and/or Cr concentration of at least about 80g/l, preferably at least about 75g/l, more preferably at least about 72g/l, e.g., about 72g/l. Typically, the Fe and/or Cr concentration of the purified iron chromium electrolyte is not adjusted upwards beyond an Fe and or concentration of about 85g/l.

The Fe and/or Cr concentration of the purified iron chromium electrolyte may be adjusted upwards during the concentration of the purified iron-chromium electrolyte. The Fe and/or Cr concentration may be adjusted upwards whilst agitating the iron chromium electrolyte, e.g., during heating of the purified iron chromium electrolyte.

Although Fe as metal is added primarily to obtain a desired Fe concentration in the purified iron chromium electrolyte, the added Fe advantageously also reduces any Fe³⁺ present in the purified iron chromium electrolyte, which may result from processing or during storage of the purified iron chromium electrolyte. This Fe³⁺ is reduced according to the following chemical reaction:



The process may include adjusting the electrical conductivity of the purified iron chromium electrolyte. Typically, prior to adjusting the electrical conductivity of the purified iron chromium electrolyte, the purified iron chromium electrolyte is cooled to a temperature which does not exceed about 30°C, preferably to a temperature which does not exceed about 25°C.

The electrical conductivity of the purified iron chromium electrolyte may be adjusted to be in the range of between about 112 mS/cm and about 140 mS/cm, preferably in the range of between about 118 mS/cm and about 135 mS/cm, more preferably in the range of between about 125 mS/cm and about 133 mS/cm, e.g., about 133 mS/cm.

Adjusting the electrical conductivity of the purified iron chromium electrolyte may be effected by the addition of hydrochloric acid, or may be affected by the addition of ammonium hydroxide, or may be affected by the addition of sulphuric acid.

The process may include subjecting the purified iron chromium electrolyte, after adjustment of its electrical conductivity, to a filtration step to ensure no solids are present in the purified iron chromium electrolyte.

5 The process of the invention can be implemented on a batch basis, a semi-batch basis, a semi-continuous basis, or as a continuous process.

 According to yet another aspect of the invention, there is provided a raw iron chromium electrolyte produced by a process as hereinbefore described.
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 According to a further aspect of the invention, there is provided a purified iron chromium electrolyte produced by a process as hereinbefore described.

 The purified iron chromium electrolyte may have a Cr concentration as
15 hereinbefore described.

 The purified iron chromium electrolyte may have an Fe concentration as hereinbefore described.

20 The purified iron chromium electrolyte may have an electrical conductivity as hereinbefore described.

 The invention extends to use of a purified iron chromium electrolyte produced by a process as hereinbefore described in an iron chromium redox flow battery.
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 The invention also extends to an iron chromium redox flow battery which includes a purified iron chromium electrolyte produced by a process as hereinbefore described.

 The invention will now be described, by way of example only, with reference to
30 the single diagrammatic drawing which shows one embodiment of a continuous process in accordance with the invention for producing an iron chromium electrolyte suitable for use in an iron chromium redox flow battery.

Referring to the drawing, reference numeral 10 generally indicates a process in accordance with the invention for producing high purity iron chromium electrolyte. The iron chromium electrolyte produced by the process 10 advantageously is sufficiently pure to allow its use in an iron chromium redox flow battery.

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The process 10 generally includes a leaching stage 12, a first filtration stage 14, a raw electrolyte purification stage 16, a concentration-adjusting stage 18, a cooling stage 20, an electrical conductivity-adjusting stage 22, and a final filtration stage 24.

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The raw electrolyte purification stage 16 comprises at least a pH adjustment stage 16.4 and an ion exchange stage 16.6. Optionally, the raw electrolyte purification stage may also comprise one or more and preferably all of an evaporation stage comprising a concentrator 16.1, a cooling stage 16.2, a heating stage 16.3, and a second filtration stage 16.5, all upstream of the ion exchange stage 16.6. Also optionally, the pH adjustment stage 16.4 may provide for cooling, in which case it is a cooling and pH adjusting stage.

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The optional components and features would be relevant in an embodiment of the process 10 in which a ferrochrome alloy feedstock to the process 10 comprises titanium. While the process is described with reference to the optional components and features, below, it should be understood that, in another expressly disclosed embodiment of the invention, the optional features are omitted.

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The leaching stage 12 is provided with a hydrochloric acid feed line 26, a particulate ferrochrome alloy feed line 28 and a hydrogen withdrawal line 30. The hydrochloric acid feed line 26 and the particulate ferrochrome alloy feed line 28 lead into, and the hydrogen withdrawal line 30 leads from, a solid-liquid fluidised bed vessel 32 which is heated.

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A slurry transfer line 34 leads from the solid-liquid fluidised bed vessel 32 to the first filtration stage 14. A solids residue withdrawal line 36 and a filtrate transfer line 38 lead from the first filtration stage 14. The filtrate transfer line 38 leads to the raw electrolyte purification stage 16, and in particular to the evaporator 16.1.

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The evaporator 16.1 is provided with a water vapour and hydrochloric acid withdrawal line 40. A concentrated raw iron and chromium electrolyte transfer 42 leads from the evaporator 16.1 to the cooling stage 16.2. A slurry transfer line 44 leads from the cooling stage 16.2 to the heating stage 16.3, and a reconstituted electrolyte solution transfer line 46 leads from the heating stage 16.3 to the cooling and pH-adjusting stage 16.4.

The cooling and pH-adjusting stage 16.4 is provided with an acid or base feed line 48 and with a slurry transfer line 50 which leads to the second filtration stage 16.5.

The second filtration stage 16.5 is provided with a solids removal line 52 and with a reconstituted electrolyte solution transfer line 54. The reconstituted electrolyte solution transfer line 54 leads to the ion exchange stage 16.6, and a purified iron chromium electrolyte transfer line 55 leads from the ion exchange stage 16.6 to the concentration-adjusting stage 18.

The concentration-adjusting stage 18 comprises a heated, agitated vessel 56 provided with a particulate iron feed line 58 and a water vapour removal line 60. For the purpose of concentration adjustment, the feed line 58 may also, or alternatively, be a feed line of one or more of water, $\text{CrCl}_3 \cdot x\text{H}_2\text{O}$, and $\text{FeCl}_2 \cdot y\text{H}_2\text{O}$, wherein x is a value from 6 to 8, preferably 6, and wherein y is a value from 2 to 4, preferably 4. In other words, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ are preferred.

A concentrated purified iron chromium electrolyte transfer line 62 leads from the vessel 56 to the cooling stage 20, and from the cooling stage 20 to the electrical conductivity-adjusting stage 22. The electrical conductivity-adjusting stage 22 is provided with a hydrochloric acid feed line 64. A purified iron chromium electrolyte transfer line 66 leads from the electrical conductivity-adjusting stage 22 to the final filtration stage 24, which is provided with a solids withdrawal line 68 and a product withdrawal line 70.

The process 10 is used to produce an iron chromium electrolyte, suitable for application as an electrolyte in an iron chromium redox flow battery. To produce the iron chromium electrolyte, particulate ferrochrome alloy and concentrated hydrochloric acid are fed respectively by means of the particulate ferrochrome alloy feed line 28 and the hydrochloric acid feed line 26 into the solid-liquid fluidised bed vessel 32. The particulate ferrochrome alloy has

an Fe content of 42% by mass, a Cr content of 50% by mass, and a D50 particle size of <0.5mm. The hydrochloric acid has a molar concentration of 6.0M and the ferrochrome alloy and the hydrochloric acid are fed into the solid-liquid fluidised bed vessel 32 at a ratio of about 155g/l. In another embodiment of the invention, the Fe content may be as low as 35% by mass and the Cr content as high as 55% by mass.

In the solid-liquid fluidised bed vessel, a slurry of the particulate ferrochrome alloy and the hydrochloric acid is fluidised and heated, e.g. by means of a steam or hot water or hot oil heating coil, to an elevated leaching temperature of about 100°C. In order to leach maximum chromium and iron from the ferrochrome alloy, the average total residence time of solids material in the solid-liquid fluidised bed vessel is about 30 minutes. This residence time is easily achieved by sizing the solid-liquid fluidised bed vessel sufficiently large, taking into account a steady state feed rate of the ferrochrome alloy and the hydrochloric acid. If desired, a plurality of solid-liquid fluidised bed vessels arranged in series may be employed.

During leaching of the iron and chromium from the ferrochrome alloy in the solid-liquid fluidised bed vessel 32, hydrogen evolves, as will be appreciated. The hydrogen is removed by means of the hydrogen withdrawal line 30. Depending on the configuration of the process 10, this hydrogen can be flared, stored for later use, or it can be used as a fuel, e.g., for heating purposes in the process 10.

Once maximum chromium and iron have been leached from the particulate ferrochrome alloy and dissolved in the hydrochloric acid, as achieved by an appropriate residence time of solids material in the solid-liquid fluidised bed vessel 32, a hot slurry of raw iron chromium electrolyte and solids residue is withdrawn from the solid liquid fluidised bed vessel 32 by means of the slurry transfer line 34 and fed to the first filtration stage 14. In the first filtration stage 14, the hot slurry is subjected to filtration to separate the solids residue from the raw iron chromium electrolyte. The solids residue is withdrawn from the first filtration stage 14 by means of the solids residue withdrawal line 36 and returned to a smelter. Alternatively, it can be discarded to a waste dump (after processing, e.g., washing, to allow dumping thereof in an environmentally safe manner). The raw iron chromium electrolyte is withdrawn as a filtrate from the first filtration stage 14 by means of the filtrate transfer line 38.

The filtrate is fed to the raw electrolyte purification stage 16 and first enters the evaporator 16.1. In the evaporator 16.1, the raw iron chromium electrolyte is concentrated by evaporation, i.e. by further heating the raw iron chromium electrolyte to its boiling temperature. Water vapour and hydrochloric acid are withdrawn by means of the water vapour and hydrochloric acid withdrawal line 40. The withdrawn water vapour and hydrochloric acid may be used to produce hydrochloric acid, which can be recycled in the process 10.

The raw iron chromium electrolyte is maintained at its boiling temperature in the evaporator 16.1 for a residence time sufficiently long to allow formation of first solid crystals. Excessive crystallisation is however not allowed. Again, this is easily achieved by sizing the evaporator 16.1 appropriately, taking into account a steady state feed rate of raw iron chromium electrolyte into the evaporator 16.1 and the time required to reach a design concentration of Fe and Cr in the concentrated iron and chromium electrolyte produced by the evaporator 16.1.

Typically, the ferrochrome alloy used in the process 10 includes some titanium, e.g., a titanium content of about 0.1% by mass. During the leaching of the particulate ferrochrome alloy in the leaching stage 12, the titanium unavoidably is also leached from the ferrochrome alloy and forms TiCl_4 . In the evaporator 16.1, at the boiling temperature of the raw iron chromium electrolyte, the TiCl_4 reacts with water to form titanium dioxide (TiO_2).

Concentrated iron and chromium electrolyte is withdrawn by means of the concentrated iron and chromium electrolyte transfer line 42 from the evaporator 16.1 and fed to the cooling stage 16.2, where the concentrated iron and chromium electrolyte is cooled to about ambient temperature. Cooling is typically effected by means of plant cooling water. In the cooling stage 16.2, TiO_2 thus crystallises with FeCl_2 and CrCl_3 to form a slurry of FeCl_2 crystals, CrCl_3 crystals and TiO_2 crystals. Typically, the FeCl_2 and CrCl_3 are respectively in the form of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$.

The slurry is withdrawn from the cooling stage 16.2 by means of the slurry transfer line 44 and fed to the heating stage 16.3, where it is heated to a temperature of about 90°C . In the heating stage 16.3, the FeCl_2 crystals and the CrCl_3 crystals redissolve, thereby forming a reconstituted electrolyte solution. Advantageously however, the TiO_2 crystals do not dissolve, or only sparingly dissolve, at the temperature in the heating stage 16.3.

A slurry of reconstituted electrolyte solution and TiO₂ crystals is transferred by means of the reconstituted electrolyte solution transfer line 46 to the cooling and pH-adjusting stage 16.4. In the cooling and pH-adjusting stage 16.4, the reconstituted electrolyte solution is cooled to a temperature of about 25°C, using plant cooling water.

The pH of the reconstituted electrolyte solution is adjusted to about 1.5 by adding an acid or base by means of the acid or base feed line 48. A cooled slurry comprising the pH-adjusted, reconstituted electrolyte solution and TiO₂ crystals is transferred from the cooling and pH-adjusting stage 16.4 to the second filtration stage 16.5, by means of the slurry transfer line 50. Most solids, including the TiO₂ crystals, are separated from the pH-adjusted reconstituted electrolyte solution in the second filtration stage 16.5, by means of filtration. The solids are removed by means of the solids removal line 52, processed if required and dumped, and the pH-adjusted, reconstituted electrolyte solution is transferred by means of the reconstituted electrolyte solution transfer line 54 to the ion exchange stage 16.6.

It will be appreciated that, in the embodiment of the invention in which the optional components and features of the purification stage 16 are omitted, the cooling and pH adjustment stage 16.4 would only be a pH adjustment stage 16.4 and the reconstituted electrolyte solution that would be fed to the stage 16.4 would be the raw iron chromium electrolyte from the first filtration stage 14 along line 38. Therefore, in the drawing, stages 16.1, 16.2, 16.3 and lines 42, 44, and 46 would be omitted and the pH adjustment would be performed on the raw iron chromium electrolyte instead of being performed on the reconstituted electrolyte solution.

In the ion exchange stage 16.6, a strong cation ion exchange resin, e.g. PurometTM MTS9600, is used to remove nickel and copper (typically introduced into the electrolyte solution by the particulate ferrochrome alloy used), providing a purified iron chromium electrolyte. The purified iron chromium electrolyte is transferred by means of the purified iron chromium electrolyte transfer line 55 to the concentration-adjusting stage 18, in which the purified iron chromium electrolyte may either be concentrated or diluted to achieve an iron and/or chromium concentration of 72 g/L.

More specifically, in the concentration-adjusting stage 18, the purified iron chromium electrolyte is heated a temperature of about 90°C to evaporate water, thereby increasing the Cr concentration of the purified iron chromium electrolyte to about 72g/ℓ. The evaporated water is removed by means of the water vapour removal line 60. Simultaneously, under agitation, particulate iron metal is fed to the agitated vessel 56 by means of the particulate iron feed line 58. The addition of the iron as metal is controlled to adjust the iron concentration of the purified iron chromium electrolyte to about 72g/ℓ. As mentioned above, as an alternative or in addition, water, $\text{CrCl}_3 \cdot x\text{H}_2\text{O}$, or $\text{FeCl}_2 \cdot y\text{H}_2\text{O}$ may be added, wherein x is a value from 6 to 8, preferably 6, and wherein y is a value from 2 to 4, preferably 4. In other words, in respect of CrCl_3 and FeCl_2 , $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ are preferred.

Concentration adjusted purified iron chromium electrolyte is transferred by means of the concentrated purified iron chromium electrolyte transfer line 62 to the cooling stage 20, where the concentrated purified iron chromium electrolyte is cooled to a temperature of about 25°C or lower, typically using plant cooling water. The cooled, concentrated, purified iron chromium electrolyte is transferred from the cooling stage 20 to the electrical conductivity-adjusting stage 22 by means of the concentrated purified iron chromium electrolyte transfer line 62. In the electrical conductivity-adjusting stage 22, hydrochloric acid is added to the concentrated purified iron chromium electrolyte by means of the hydrochloric acid feed line 64, thereby adjusting the electrical conductivity of the purified iron chromium electrolyte upwards to about 133 mS/cm.

Purified iron chromium electrolyte is transferred by means of the purified iron chromium electrolyte transfer line 66 from the electrical conductivity-adjusting stage 22 to the final filtration stage 24, where the purified iron chromium electrolyte is subjected to a final filtration step to remove any remaining solids. The solids are withdrawn by means of the solids withdrawal line 68 and dumped and a product, that is, purified iron chromium electrolyte filtrate with the desired Cr concentration, Fe concentration and electrical conductivity, is removed from the final filtration stage 24 by means of the product withdrawal line 70.

The process 10, as illustrated, advantageously produces a purified iron chromium electrolyte from ferrochrome alloy, which is suitable for use in an iron chromium redox flow battery. The iron chromium electrolyte is advantageously produced directly from ferrochrome

alloy thus eliminating the need for separation and purification of iron and chrome individually. This has major cost, health, and safety benefits in that nowhere in the process 10, as illustrated, is Cr^{6+} produced.

CLAIMS

1. A process for producing an iron chromium electrolyte, the process including
leaching iron and chromium from a ferrochrome alloy at an elevated leaching
5 temperature, using hydrochloric acid, to produce a raw iron chromium electrolyte comprising
dissolved iron and dissolved chromium; and
purifying the raw electrolyte to produce a purified iron chromium electrolyte.
2. The process according to claim 1, wherein the ferrochrome alloy has
10 an Fe content of between about 35% by mass and about 45% by mass, preferably
between about 37% by mass and about 44% by mass, more preferably between about 39% by
mass and about 44% by mass, e.g., about 42% by mass; and
a Cr content of between about 45% by mass and about 60% by mass, preferably between
about 46% by mass and about 54% by mass, more preferably between about 48% by mass and
15 about 52% by mass, e.g., about 50% by mass.
3. The process according to claim 1 or claim 2, wherein the ferrochrome is a
particulate ferrochrome alloy having a particle size with a D50 of between about 0.5mm and
about 1.5mm, preferably between about 0.5mm and about 1.2mm, more preferably between
20 about 0.5mm and about 1mm.
4. The process according to any one or claims 1 to 3, wherein the hydrochloric acid
is at a molar concentration of between about 3M and about 8M, preferably about 6.0M.
- 25 5. The process according to any one of claims 1 to 4, wherein a ratio of ferrochrome
alloy to hydrochloric acid is in the range of about 100g/ℓ to about 200g/ℓ, preferably in the range
of about 120g/ℓ to about 180g/ℓ, more preferably in the range of about 140g/ℓ to about 170g/ℓ,
e.g., about 155g/ℓ.
- 30 6. The process according to any one or claims 1 to 5, wherein the elevated leaching
temperature is between about 80°C and about 100°C, preferably between about 85°C and about
95°C, more preferably between about 95°C and about 100°C, e.g., about 95°C.

7. The process according to any one of claims 1 to 6, wherein the iron and chromium are leached from the ferrochrome alloy for a period of between about 30 minutes and about 24 hours, preferably between about 8 hours and about 14 hours, more preferably between about 4 hours and about 12 hours, e.g., for a period of about 14 hours.
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8. The process according to any one of claims 1 to 7, wherein the iron and chromium are leached from the ferrochrome alloy in a solid-liquid fluidised bed.
9. The process according to any one of claims 1 to 8, wherein purifying the raw iron chromium electrolyte comprises removing Ni and Cu, either simultaneously or separately, from the raw electrolyte by subjecting the raw electrolyte to a pH adjustment step and, subsequently, to an ion exchange step, wherein
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- in the pH adjustment step, the pH of the raw iron chromium electrolyte is adjusted to between 0.0 and 2, e.g. about 1.5 by using a base or an acid; and
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- in the ion exchange step, the raw iron chromium electrolyte is contacted with a strong cation ion exchange resin.
10. The process according to any one of claims 1 to 9, which includes concentrating or diluting the purified iron chromium electrolyte to a Cr and/or Fe concentration of at least about 80g/ℓ, preferably at least about 75g/ℓ, more preferably at least about 72g/ℓ.
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11. The process according to claim 10, wherein the purified iron chromium electrolyte is concentrated by heating the purified iron chromium electrolyte to evaporate water or by using an iron and/or chromium rejecting membraned process
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12. The process according to any one of claims 1 to 11, which includes adjusting the Fe and/or Cr concentration of the purified iron chromium electrolyte upwards to an Fe and/or Cr concentration of at least about 80g/ℓ, preferably at least about 75g/ℓ, more preferably at least about 72g/ℓ, by
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- adding Fe as metal, or Fe as a salt such as iron sulphate or iron chloride; and/or
- adding Cr as metal, or as a Cr salt such as chromium sulphate or chromium as chromium chloride.

13. The process according to any one of claims 1 to 12, which includes adjusting the electrical conductivity of the purified iron chromium electrolyte to be in the range of between about 112 mS/cm and about 140 mS/cm, preferably in the range of between about 118 mS/cm and about 135 mS/cm, more preferably in the range of between about 125 mS/cm and about 133 mS/cm, e.g., about 133 mS/cm by cooling the purified iron chromium electrolyte to a temperature which does not exceed about 30°C, preferably to a temperature which does not exceed about 25°C, and by adding hydrochloric acid, ammonium hydroxide, or sulphuric acid to the cooled purified iron chromium electrolyte.
14. A process for producing a raw iron chromium electrolyte, the process including leaching iron and chromium from a ferrochrome alloy at an elevated leaching temperature, using hydrochloric acid, to produce said raw iron chromium electrolyte comprising dissolved iron and dissolved chromium.
15. A purified iron chromium electrolyte produced according to the process according to any one of claims 1 to 13, or a raw iron chromium electrolyte produced according to the process according to claim 14.
16. Use of the purified iron chromium electrolyte produced by a process according to any one of claims 1 to 13 as an electrolyte of an iron chromium redox flow battery.
17. An iron chromium redox flow battery which includes a purified iron chromium electrolyte produced according to the process according to any one of claims 1 to 13.