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(54) Title: A METHOD AND COMPOSITION FOR SEQUESTRATION OF ARSENIC

(57) Abstract: There is provided a method and composition for sequestration of arsenic, the method comprising melting an arsenic-containing material in the presence of iron oxide and glass, and yielding a resulting glass incorporating arsenic. The resulting glass has an arsenic content comprised in a range between 1 and 25% w/w and an iron content comprised in a range between 8 and 20% w/w.

TITLE OF THE INVENTION

A method and composition for sequestration of arsenic

FIELD OF THE INVENTION

[0001] The present invention relates to sequestration of arsenic. More specifically, the present invention is concerned with vitrification of arsenic adsorbed on iron oxide.

BACKGROUND OF THE INVENTION

[0002] In 1834 Robert Bunsen discovered that arsenious oxide, a highly toxic material, could be rendered innocuous by contacting with iron oxide. The mechanism involved in this adsorption has been studied extensively as summarized in Gallegos-Garcia *et al.* (Mineral Processing & Extractive Metall. Rev. 33: 301-315, 2012). Various forms of iron oxides, such as hematite (Fe_2O_3), are reported to share structural oxygen atoms with arsenious oxides in angelellite-like local clusters.

[0003] These principles have been converted into industrial methods for the treatment of anthropogenic sources of arsenic such as flue dusts from smelters or naturally occurring contamination of water tables. The end products after adsorption of arsenic on hematite are found to be able to not release the arsenic, either trivalent or pentavalent as per standard acetic acid leaching procedure: EPA 1311 Toxicity Characteristic Leaching Procedure (TCLP). However, extreme pH condition or mechanical attrition can disperse this fixed arsenic in the environment.

[0004] Therefore, it has appeared desirable to complete this capture of arsenic by hematite by grouping the particulates obtained after adsorption into a macroscopic glass structure. Sequestration of arsenic by glass formation is a known procedure (US Patent 8,998,790). It was made possible by the thermal stability of calcium arsenate at a temperature where glass forming elements can lead to stable and homogeneous glass.

[0005] There is still a need in the art for a method and a composition for sequestration of arsenic.

SUMMARY OF THE INVENTION

[0006] More specifically, in accordance with the present invention, there is provided a method for the vitrification of arsenic of an arsenic-containing material, comprising melting the arsenic-containing material in the presence of iron oxide and glass, and yielding a resulting glass incorporating arsenic.

[0007] There is further provided a stable glass composition, with an arsenic content comprised in a range between 1 and 25% w/w and an iron content comprised in a range between 8 and 20% w/w.

[0008] Other objects, advantages and features of the present invention will become more apparent upon reading of the following non-restrictive description of specific embodiments thereof, given by way of example only with reference to the accompanying drawings.

DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

[0009] The present invention is illustrated in further details by the following non-limiting examples.

[0010] There is generally provided a method comprising the incorporation of arsenic complexed on iron oxide into a homogeneous and stable glass phase and a stable glass composition sequestering arsenic as an iron/arsenic complex in the long-term.

[0011] In the arsenic-containing materials, the arsenic can be of various forms, such as pure arsenious oxide (95% w/w As_2O_3) or flue dusts from a copper smelter. The arsenious oxide (As_2O_3) content of the arsenic-containing materials is comprised between about 5 and about 95% w/w (unless otherwise indicated, the percentage are percentages in weights, i.e. % w/w).

[0012] The selected iron oxide-containing material comprises at least 15 % w/w iron oxide. The iron oxide can take a range of forms, such as near pure (95% w/w) Fe_2O_3, or raw hematite, such as raw hematite found in Fermont, Qc, Canada for example with the following composition: Fe_2O_3: 45.6% w/w; SiO_2: 53.0% w/w: CaO: 0.8% w/w; K_2O: 0.25% w/w; NiO: 0.1 % w/w; ZnO: 0.05% w/w.

[0013] The arsenic and the iron oxide-containing materials may be first reduced in size to particulates, for example to particulates 80% below 120 mesh, before mixing them together, using for example a ribbon mixer or any other powder mixer as known in the art, to obtain a mixture with a iron oxide (Fe_2O_3) content between 8 and 20% w/w.

[0014] A glass material, such as glass, recycled glass or glass-forming elements, with a silica content comprised in the range between 40 and 80% w/w, is then added, so as to obtain a mixture with the arsenic and the iron oxide-containing materials, with a target ratio of oxides as a starting feed for fusion. A typical starting feed for fusion may contain 17% w/w arsenious oxide (As_2O_3), 69% w/w recycled glass and 14% w/w iron oxide (Fe_2O_3) for example. Recycled glass has a typical composition as follows: Fe: 0.2% w/w; Mg, 0.9% w/w; Ca:

7.8% w/w; Si: 35.2%; Al: 1.0%; Na: 9.35%; K: 0.5%; B: 0.03% w/w for example.

[0015] In the starting feed for fusion, the arsenious oxide (As_2O_3) content may range from about 1% w/w to about 20% w/w, the loss of arsenic by volatilization during fusion remaining below 3.0% w/w and the acetic acid leaching of the resulting glass is at around 1 ppm As, well below the 5 ppm norm (EPA Code of Federal Regulations, Title 40 – Protection of Environment, Volume 27, Section 261.24, EPA HW No. 1). As to the iron, under the form of iron oxide (Fe_2O_3), the content thereof in the starting feed for fusion may range from about 6% w/w to about 15% w/w without experimenting fusion problems or significant volatilization of arsenic during the fusion or during leaching of the vitrified arsenic.

[0016] The amount of glass in the starting feed for fusion is adjusted depending on the nature of the glass used, i.e., recycled glass or glass-forming elements, and of the composition of the arsenic and the iron oxide-containing materials used.

[0017] If hematite is used as the iron oxide source, with high silica content as described above in the case of the Fermont ore for example, small amounts of alkali or alkaline earth oxides (Na_2O, CaO, MgO) may be added so as to bring these silica impurities near a typical composition of recycled glass as given hereinabove (see Example 7 below for instance).

[0018] The raw mixture of arsenic, iron oxide and glass can be pelletized before melting, in order to limit dust emissions during the loading of the mixture in crucibles for example. Then fusion is done at atmospheric pressure at a temperature of at least 900°C, for example in a range comprised between 950°C and 1250°C, and yields a black glass of very homogeneous composition resulting from a very homogenous blending of the components of the feed for fusion. Dust and fumes emitted during the fusion may be collected and recycled.

[0019] Without limitations to the scope of this invention, the following examples illustrate embodiments of the present invention.

[0020] Example 1

[0021] A mixture of 20.4 g of As_2O_3 (analytical grade), 51.0 g of recycled glass (80 -120 mesh), 1.1 g Na_2SiO_3, 5.1 g Na_2CO_3 and 22.0 g Fe_2O_3 from an hematite raw ore containing 46.3% Fe_2O_3 and 52.5% SiO_2 was melted in a refractory crucible by heating in an electrically heated furnace for one and a half hour at 1250°C. After cooling, the resulting glass had the following composition: As: 15.4%; Si: 24.5%; Na: 7.6%; Ca: 4.1% and Fe 7.57%. This indicated a loss of 2.6% of the arsenic by volatilization in the course of the fusion. Standard leaching tests with acetic acid gave 3.07 ppm leaching, confirming the stability of this resulting glass.

[0022] Example 2:

[0023] An experiment similar to Example 1 was conducted except that instead of using recycled glass, glass forming elements, i.e. silica and alkali, were used. The formulation of starting feed for fusion mixture was: As_2O_3: 19.0%; Recycled glass: 0%; SiO_2: 38%; Na_2SiO_3: 1.1%; Na_2CO_3: 21.0%; Fe_2O_3: 20%.

[0024] There was a 2.75% loss of arsenic during the glass formation, and the acetic acid leaching of the resulting glass, at 1.46 ppm, confirmed the stability of the resulting glass.

[0025] Example 3

[0026] An experiment was performed along similar conditions than those of Example 2, i. e. using glass forming elements, but with a starting feed for fusion mixture deprived of iron oxide, i.e. with the following starting feed for fusion: As_2O_3: 17.8%; recycled glass: 0%; SiO_2: 53.3%; Na_2SiO_3: 1.0%; Na_2CO_3: 25.8%; Fe_2O_3: 0%. An arsenic loss of 12.1% during fusion and a leaching by acetic acid of 426 ppm As were indications that the glass, obtained in absence of iron oxide in the starting feeding mixture, did not efficiently retain or stabilize arsenic.

[0027] Example 4

[0028] The procedure described in Example 1 was repeated, except that the temperature of fusion for glass formation was 900°C instead of 1250°C and the heating duration was two hours instead of one and a half hour. A glass was formed. This resulting glass showed a low release of arsenic when submitted to acetic acid leaching (1.5 ppm). However, because of its viscosity, it could not be casted and it retained significant amounts of bubbles, i.e. was not homogenous.

[0029] Example 5

[0030] Flue dusts from a copper smelter containing 76.4% As_2O_3; 14.6% PbO; 2.5% Sb_2O_3; 0.3% TeO_2 and 0.8% CuO were used as the arsenic-containing material. A mixture comprising 35 g of these flue dusts with 55 g of recycled glass, 2.9 g Na_2CO_3 and 20 g of Fe_2O_3, i.e. resulting in a starting feed for fusion comprising 31% w/w flue dust, 49% w/w recycled glass, 2.5% w/w Na_2CO_3 and 17.7% w/w Fe_2O_3, was prepared and melted at 1250°C for one and a half hour. The resulting glass was submitted to lixiviation test with acetic acid. It was noted that the leaching of arsenic was low, at 1.2 ppm, and also that the other elements present in the starting feed for fusion were kept essentially sealed within the glass during the acetic leaching, with Pb at 0.53 ppm L, Sb at 0.18

ppm, Te at 0.01 ppm and Cu at 0.08 mg/L in the acetic leacheate.

[0031] Example 6

[0032] Using the parameters of Example 1, several samples of glasses were prepared in order to establish a ratio of arsenious oxide to hematite allowing obtaining a resulting glass that retains arsenic efficiently as per the acetic acid test. Starting with a starting feed for fusion containing 13% w/w As, 24.5% w/w Si, 6.5% w/w Na, 5.22% w/w Ca and 9.38% w/w Fe, the resulting glass had the following composition: As: 12.3% w/w; Si: 25.0% w/w; Na: 6.65% w/w; Ca: 5.34% w/w and Fe: 9.58% w/w. On treatment with acetic acid, 1.98 ppm of arsenic was leached out, well below the norm (EPA Code of Federal Regulations, Title 40 – Protection of Environment, Volume 27, Section 261.24, EPA HW No. 1). Operating with a starting feed for fusion where the iron content was reduced to 6.03%, the leaching of arsenic from the resulting glass (6.14% Fe) was up to 4.5 ppm. Formulations still leaner in iron gave acetic leachates above 5% As. A level of at least about 8% iron in the starting feed for fusion, with about 13% As, was found to yield an efficient sequestration of arsenic.

[0033] Example 7

[0034] Flue dusts from a copper smelter having the following composition: As: 60.6%; Cd: 0.24%; Cu: 0.41%; Fe: 0.24%; Mg: 0.47%; Mn: 0.13%; Pb: 1.11%; Bi: 0.6%; Sb: 1.24%; Te: 0.25%; Se: 0.10%, S: 1.11% and Zn: 0.68% were used as the arsenic-containing material.

[0035] An homogeneous mixture of 5.14 Kg of flue dust, 6.43 Kg of raw hematite (40% Fe_2O_3), 9.86 Kg of silica (crystalline silica, 99% SiO_2) and 8.57 Kg of sodium carbonate Na_2CO_3 (light variety, i.e. containing contains less than 0.5% sodium chloride) were blended in a ribbon mixer with 12% of the weight of the solid as added water. Under these conditions, the solid mixture was pelletized into large (several centimetres, i.e. in a range between 1 and 10 cm) lumps. After drying at 100°C, these lumps could be loaded to a 300 liter pre-heated crucible heated at 1200°C without significant dust emission. The fusion was completed at this temperature by heating for one hour in a gas fired furnace. The resulting glass was casted in a sand-lined mold.

[0036] The resulting glass weight was 24.5 Kg, and showing an As content of 10.96%. The test TCLP, EPA 1311 with acetic acid indicated a leaching at the level of 0.11 ppm, the norm being 5.0 ppm. This result confirms the very high stability of the confinement of arsenic in the glass. This stability was extended to other contaminants in the starting flue dust, the leachate from EPA 1311 containing 0.0015 ppm Cd, 0.11 ppm Cu, 0.018 ppm Pb, 0.0065 ppm Sb, 0.0043 ppm Se and 0.0060 ppm Te.

[0037] There is thus provided a method for the vitrification of arsenic, comprising the fusion of arsenic in the presence of iron oxide and glass.

[0038] The iron oxide may be hematite or an hematite ore containing more than 15% Fe_2O_3. The glass is a glass or recycled glass or glass formed *in situ* from silica and alcalis and containing from 40 to 80% w/w silica. The source of arsenic may be oxides of arsenic, or flue dusts containing from 5% to 95% w/w As_2O_3 along with other contaminants such as arsenides, lead, antimony, bismuth, cadmium, selenium or tellurium compounds, or combinations of these elements. These compounds can be sequestred.

[0039] The mixture of arsenic, iron oxide and high silica glass, i.e. the feed for fusion, comprises between 1 and 20% w/w As_2O_3, for example about 13% w/w As_2O_3, and between 6 and 15% w/w Fe_2O_3, for example between 8 and 15% w/w Fe_2O_3.

[0040] The feed for fusion is melted at a temperature of at least 900°C, for example in a range comprised in a range between 950 and 1250°C, at atmospheric pressure, for about 1 hour, to allow formation of an homogeneous glass. Glass at the end of fusion is 50-60% of the total weight, the remaining being mainly As_2O_5, Fe_2O_3, PbO and CaO.

[0041] The iron content in the resulting glass varies from about 8 to about 20% w/w, and its arsenic content, under the form of arsenic pentoxide As_2O_5, varies from about 1 to about 25% w/w, for example between 1 and 20% w/w.

[0042] While it was believed in the art that ferric arsenate ($FeAsO_4$), a ferric salt of arsenic, decomposes at melting, with a boiling point at 614°C as stated by a supplier American Elements, Inc. for example, the present invention provides glass formation of an iron oxide/arsenic oxide complex at temperatures required for glass formation without decomposition nor large volatilization of arsenic.

[0043] Thus incorporation of arsenic-iron oxide adsorbate into a glass structure is obtained, which allows long-term efficient sequestration of the arsenic and without risk of dispersion either by chemical leaching or mechanical attrition for example.

[0044] The scope of the claims should not be limited by the embodiments set forth in the examples, but should be given the broadest interpretation consistent with the description as a whole.

Claims

1. A method for the vitrification of arsenic of an arsenic-containing material, comprising melting the arsenic-containing material in the presence of iron oxide and glass, and yielding a resulting glass incorporating arsenic.

2. The method of claim 1, comprising selecting an iron oxide-containing material containing at least 15% w/w iron oxide; selecting a glass material with a silica content of at least 40% w/w; mixing the arsenic-containing material, the iron oxide-containing material and the glass material into a mixture and melting the mixture at a temperature of at least 900˚C, at atmospheric pressure.

3. The method of any one of claims 1 and 2, wherein said melting the mixture is performed at a temperature comprised in a range between 950 and 1250˚C.

4. The method of claim 2, wherein said selecting the iron oxide-containing material comprises selecting one of: i) hematite and ii) hematite ore.

5. The method of any one of claims 2 to 4, wherein said selecting the glass material comprises selecting one of: i) high silica glass, ii) recycled glass and iii) glass forming elements.

6. The method of any one of claims 2 to 5, wherein the mixture comprises between 1 and 20% w/w arsenious oxide and between 6 and 15% w/w iron oxide.

7. The method of any one of claims 2 to 6, wherein the arsenic-containing material comprises arsenious oxide in a range between 5 and 95% w/w.

8. The method of any one of claims 2 to 7, wherein the arsenic-containing material comprises arsenious oxide in a range between 5 and 95% w/w and contaminants, the method yielding vitrification of the contaminants into the resulting glass.

9. The method of any one of claims 2 to 8, wherein the arsenic-containing material comprises arsenious oxide in a range between 5 and 95% w/w and contaminants, the method yielding vitrification of the contaminants into the resulting glass, the contaminants being at least one of: arsenides, lead, antimony, bismuth, cadmium, selenium or tellurium compounds, and combinations thereof.

10. The method of any one of claims 2 to 9, wherein the resulting glass comprises arsenic in a range between 1 and 25% w/w.

11. The method of any one of claims 2 to 10, wherein the resulting glass comprises arsenic in a range between 1 and 20% w/w.

12. The method of any one of claims 2 to 11, wherein the resulting glass comprises iron in a range between 8 and 20 % w/w.

13. The method of claim 1, comprising mixing the arsenic-containing material, an iron oxide-containing material and a glass material into a mixture comprising between 1 and 20% w/w arsenious oxide and between 6 and 15% w/w iron oxide and melting the mixture at a temperature comprised in a range between 950 and 1250˚C, at atmospheric pressure.

14. The method of any one of claims 1 and 13, wherein the arsenic-containing material comprises arsenious oxide in a range between 5 and 95% w/w, said method comprising selecting an iron oxide-containing material containing at least 15% Fe_2O_3 and selecting a glass material comprising silica in a range between 40 to 80% w/w; the resulting glass having an arsenic content comprised in a range between 1 and 25% w/w.

15. A stable glass composition, with an arsenic content comprised in a range between 1 and 25% w/w and an iron content comprised in a range between 8 and 20% w/w.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2016/050390

A. CLASSIFICATION OF SUBJECT MATTER
IPC: ***A62D 3/32*** (2007.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC: A62D 3/32 (2007.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Documents cited in the documents listed in C, and in the Description.

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)
Canadian Patents Database; INTELLECT; Quester Orbit; Google Scholar

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 8,998,790 B2 (LALANCETTE ET AL) 7 April 2015 (07-04-2015)	1
Y		1 – 15
X	US 2011/0144408 A1 (GRUBER ET AL) 16 June 2011 (16-06-2011)	1
Y		1 – 15
A	US 2009/0023973 A1 (LOWERY ET AL) 22 January 2009 (22-01-2009)	1 - 15

☐ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

*	Special categories of cited documents:
"A"	document defining the general state of the art which is not considered to be of particular relevance
"E"	earlier application or patent but published on or after the international filing date
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O"	document referring to an oral disclosure, use, exhibition or other means
"P"	document published prior to the international filing date but later than the priority date claimed
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"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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