



(51) International Patent Classification:

C03C 1/00 (2006.01) C03C 1/04 (2006.01)

C03C 3/12 (2006.01) C03C 4/08 (2006.01)

C03C 3/16 (2006.01) B09B 3/00 (2022.01)

C03C 3/17 (2006.01)

(21) International Application Number:

PCT/IN2021/051196

(22) International Filing Date:

22 December 2021 (22.12.2021)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

202011056180 23 December 2020 (23.12.2020) IN

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, IT, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH,

GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

Published:

- with international search report (Art. 21(3))
- in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE

(54) Title: A METHOD FOR SAFE DISPOSAL OF ARSENIC RICH SLUDGE OBTAINED FROM TREATMENT OF CONTAMINATED GROUNDWATER AND ITS UTILIZATION IN DEVELOPING HEAT PROTECTIVE GLASS

(57) Abstract: Present invention deals with the incorporation of As contaminated sludge obtained from water filtration into glass matrix to develop heat absorbing properties within the glass. The glass composition is optimized incorporating waste sludge in order to reduce near Infrared (NIR) transmission (~1000-1100 nm). A phosphate base glass composition has been melted incorporating different percentage (5-20 wt. %) of As contaminated sludge (up to 20 wt. %) to produce glass. Significant chemical durability has also been observed after 14 days of thermal cycle in distilled water at 75 oC for 8 h duration. No leaching of hazardous element (As, Fe etc.) is detected in distilled water from the glass containing 5 and 15 wt.% arsenic containing sludge by ICP AES. UV-Vis-NIR spectra suggest possibility of 30 % reduction in optical transmission at NIR region than visible region and this indicates feasibility of preparation heat shielding glass (due to low transmission at above 1000 nm). Thus, arsenic contaminated sludge can be trapped into the glass which has high heat protective properties. The potential use of this glass can be in window panel significantly reducing air-conditioning and lighting load in the building. Further, this glass can of use in glare cutting application and other application.

**A METHOD FOR SAFE DISPOSAL OF ARSENIC RICH SLUDGE OBTAINED
FROM TREATMENT OF CONTAMINATED GROUNDWATER AND ITS
UTILIZATION IN DEVELOPING HEAT PROTECTIVE GLASS**

5 FIELD OF THE INVENTION

The present invention relates to a method for safe disposal of arsenic rich sludge obtained from treatment of contaminated groundwater and its utilization in developing heat protective glass. Particularly, present invention relates to the development of different usable glass products such as color glasses, decorative glass ware, table glass ware etc.

10 BACKGROUND AND PRIOR ART OF THE INVENTION

Arsenic contamination of groundwater is a form of groundwater pollution which is often due to naturally occurring high concentrations of arsenic in deeper levels of groundwater. It is a high-profile problem due to the use of deep tubewells for water supply in the Ganges Delta, causing serious arsenic poisoning to large numbers of people. A 2007 study found that over 137 million people in more than 70 countries are probably affected by arsenic poisoning of drinking water. The problem became serious health concern after mass poisoning of water in Bangladesh. There are several ways to remove arsenic from the ground water in order to make suitable for human consumption. However, arsenic contaminated sludge after filtration is discharged in land creating serious contamination of surface water. Thus, it is very important to treat the contaminated sludge in an environmentally friendly manner.

Reference may be made to Patent No *GB2371542A*, wherein a waste heavy metals like Cd, Pb, Ba, Zn, Hg, Ni, As, Cr, Se are incorporated into a glass matrix from its salts by introducing a suitable glass former (Phosphate/borosilicate) and iron salt. The glass precursors along with these heavy metal salts/ oxides were heated at a certain temperature. All over 20-45% metal oxides were incorporated into glass matrix and the obtained glass was chemically durable.

Drawbacks are observed that the invention relates to encapsulation of heavy metals salt into glass matrix without discussing any application of final glass containing waste heavy metals salts/ oxide.

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Reference may be made to the Patent No. CN103265171B, wherein an arsenious waste curing method is revealed. The arsenious waste curing method comprises the following steps of: (1) grinding arsenious waste into powder, adding into iron, boron and phosphorous basic glass ingredients and a stabilizer, and uniformly mixing raw materials and drying; and (2) placing the dried raw materials into a stainless steel mould, heating to 400-500 °C at a constant speed within 0.8-1.2 hours, and insulating for 1-2 hours, wherein intensity of pressure in the stainless steel mould is maintained to be 10-12Mpa all the time in the heating process; and founding, homogenizing, then carrying out natural cooling to room temperature, taking out the mould, and demoulding, thus the solid arsenic crystal product is obtained. The invention also provides a solid arsenic crystal product generated by the arsenious waste curing method. Arsenic curing rate of the arsenious waste curing method is high, and the produced cured product can be used for making a building or decorative material.

Drawbacks are observed that the invention relates to a curing method of arsenious waste. The cured product is not glass and same will not be useful in light transmission purpose.

Reference may be made to the Patent CN107311455A, wherein a method for preparing Arsenic-Containing Cured Glass by Arsenic-Containing Waste Slag is revealed. The invention discloses a method for preparing arsenic-containing cured glass by arsenic-containing waste slag. Arsenic-containing waste slag, copper melting waste slag, a silicon-based material and boracic acid are subjected to mixed ball milling is performed followed by sieving. The mixed material is put into a fire-resistant mold and solid-phase reaction is performed under a certain temperature condition. Then, the materials are taken out to be cooled in the high-temperature state. The cured glass with uniform color and luster, high hardness and smooth surface is obtained. The obtained cured glass meets the requirements of the general inorganic glass materials for industry. The method has the advantages that the waste and abandoned copper slag and dangerous waste of arsenic-containing waste slag in industry are used to be converted into curing glass with the industrial utilization value through directional regulation and control. The quantity reduction and secondary resource utilization of the copper slag can be realized. The harmless disposition goal of the arsenic-containing waste slag is achieved and waste materials are changed into valuable materials. A green and sustainable path is opened up for the copper slag and arsenic pollution treatment in copper melting industry.

Drawbacks are observed that the invention discloses a method for preparing arsenic-containing cured glass by arsenic-containing waste slag. The transmission of glass product is not presented. Moreover, the application of the products is not revealed.

- 5 Reference may be made to the Patent US5880045A, wherein lead-free phosphate glass is prepared for radioactive and hazardous mixed nuclear waste form by melt quench technique at around 900° C and ceramic form can be achieved at around 400-425°C. Leaching test was carried out at pH 7 at 90° C for 30 days. Up to 20 mol% of metal oxides was encapsulated into the vitrified glass. An Independent claim is also included for a lead-free glass-ceramic composite
- 10 comprising 20 to 50 mole % tin oxide and 30 to 70 mole % phosphate and 0.5 to 35 wt. % fly ash. The waste glass is durable and can withstand delocalisation by ecological forces. The fly ash used in the glass-ceramic composite comprises 3 to 6 mole % SiO₂, 3 to 6 mole % Al₂O₃, 3 to 8 mole % silicon oxide, 0.5 to 2 mole % iron (III) oxide, 3 to 6 mole % K₂O up to 1.5 mole % and up to 0.5 mole % MgO.
- 15 Drawbacks are observed that the invention discloses a method for preparing arsenic-containing cured glass by arsenic-containing waste slag. The transmission of glass product is not presented. Moreover, the application of the products is not revealed.

- Reference may be made to Patent US5960368A, wherein a suitable method of reducing the overall volume of a waste material, comprised of organic wastages and hazardous radioactive waste is described and converting it into solid glass or ceramic product for safe and economical disposal. The waste products which contain organic carbon were subjected to acid dosing at a certain contact temperature (140-210° C) in order to eliminate the exhaust gasses and then concentrated wastes were immobilized into phosphate glasses at 1050-1300° C. Standard
- 20 leaching tests were carried out and the leaching results were below EPA limit. Four types of hazardous wastes are involved with the process -Wastes(I) treated are low level radioactive or low level mixed wastes comprising job control waste, ion exchange resins or reactor coolant system cleaning streams (claimed). Organic compound (II) is neoprene, polyethylene, polypropylene, PVC, cellulose, EDTA, tributyl phosphate, polystyrene, oils and/or resins
- 25 (claimed) and the radioactive (III) or hazardous (IV) waste contains uranium, plutonium, thorium, caesium, strontium, silver, zinc, nickel, mercury or arsenic etc.
- 30

Drawbacks are observed that the invention discloses a method for handling organic wastages and hazardous radioactive waste and converting it into solid glass or ceramic product for safe and economical disposal. Application of glass is not revealed in the invention.

5 Reference may be made to Patent US3365578A, wherein a glass with melting point 850 -1100 °C comprising oxides (a) suitable for glass-forming and waste (b) loading within 20-50% by weight. Oxides (a) may be of Ca, Na, K, Mg, Pb, Mo, Zn, Al or Fe or B, P or Si which may be in the form of borates, phosphates or silicates. The term "waste oxides" is defined as the mixture of oxides in the effluent or waste from treatment to remove U and Pu from irradiated metallic U
10 fuel having burn-up greater than 3000 MW d/t. The oxides may initially be present as nitrates. Waste oxides comprise oxides of U, alloying additions, fission products and canning material and may include oxides of Ba, Ce, Cs, La, Mo, Nd, Pd, Pr, Rh, Ru, Sm, Sr, Tc, Te, Y, Zr, Fe, Al; smaller amounts of Ag, Eu, Pm, Rb, Cr, Ni, Mg and Si oxides may also be present.

15 Drawbacks are observed that the invention discloses a method for glass preparation encapsulating various oxide waste. This is not related with arsenic disposal process. Further, application of glass is not revealed in the invention.

Reference may be made to Patent MX2017008577A, wherein a method and Composition for
20 Sequestration of Arsenic is presented. 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.

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Drawbacks are observed that the invention discloses a method and composition for sequestration of arsenic is presented. the method comprising melting an arsenic-containing material in the presence of iron oxide and glass, and yielding a resulting glass incorporating arsenic. The invention relates only development of glass containing arsenic and iron and further application
30 of the resultant glass is not discussed.

Reference may be made to Patent US4988376A, wherein Process for immobilizing the lead in a solid waste consists essentially of forming a vitrified mass containing the lead is described. A fluxing agent is added to lower the temperature at which melting occurs and a reducing agent added to reduce precious metals and allow them to be recovered. If the original waste contains insufficient silica for verification to occur then further silica is added. One of the prior advantages of this process is the immobilization of lead in waste material particle soil contaminated with heavy metals. The vitrified lead containing material produced may then be used as a shielding material for radioactive waste. Process also permits the recovery of precious metals from the waste. The vitrified lead containing material produced may then be used as a shielding material for radioactive waste.

Drawbacks are observed that the invention relates a process for immobilizing the lead in a solid waste. A fluxing agent is added to lower the temperature at which melting occurs and a reducing agent added to reduce precious metals and allow them to be recovered. This is not related with arsenic disposal method and developing product.

Reference may be made to Patent RU2432631C1, wherein immobilization method of liquid radioactive waste from power industry to ceramics is described which involves concentration of radioactive solutions and mixing with phosphate matrix and further heat treatment. Waste concentrated to the level of high-active waste is calcinated after having been mixed with bone phosphate till ceramic sinter is obtained. Sinter is capsulated into glass. All the process stages are performed in one and the same reaction vessel. Vitrification is performed at temperatures not exceeding 1000° C. Invention allows obtaining stable mineral-like structural forms: kosnarite $[(Na, Cs, Sr, Ln)(Zr, An, Fe)_2(PO_4)_3]$, monazite $[(Ln, An)PO_4]$, zirconium oxide $[(Zr, Ln, An)O_2]$, which have essentially large capacity approximately in relation to all radionuclides.

Drawbacks are observed that the invention relates to a process for immobilization method of liquid radioactive waste from power industry to ceramics which involves concentration of radioactive solutions and mixing with phosphate matrix and further heat treatment. This is not related with arsenic disposal method.

Reference may be made to Patent EP1946858A4, wherein a method of producing glass articles is revealed. The inventive method consists in melting oxides and other raw materials in a glass

melting furnace in order to produce molten glass and conveying the molten glass from the melting furnace to moulds in which the articles are formed as the glass solidifies. The invention is characterised in that it comprises the following steps consisting in: supplying the glass melting furnace with sludge from wastewater treatment plants, comprising determined concentration of oxides; and adding suitable amounts of corresponding compounds to the melting furnace in order to obtain a determined total end composition of the aforementioned oxides, such that the oxide composition of the resulting article corresponds to that of a rock having a low melting temperature and low viscosity within the working temperature range of glass.

Drawbacks are observed that the invention relates to a method of producing glass articles. This is not related with arsenic disposal method.

Reference may be made to Patent RU2203513C2, wherein recovery of radioactive liquid wastes is done by immobilizing the wastes by vitrifying in glass system. Proportion of glass-forming compound ingredients is as follows, mass percent: Na₂O:21-27, B₂O₃:3-9, P₂O₅:32-50, Al₂O₃:14-28; total mass percent of metal oxides contained in wastes, including Al₂O₃:19-35. Homogeneous glass was produced with melting temperature < 1050° C.

Drawbacks are observed that the invention relates to a method for recovery of radioactive liquid wastes and immobilizing the wastes by vitrifying in glass system. This is not related with arsenic disposal method.

Reference may be made to Patent SU1087091A3, wherein a glass based upon a aluminum phosphate, or other trivalent metal were used for encapsulation of high level radioactive nuclear waste. When containing a controlled amount of those elemental oxides found in a typical nuclear waste, the waste-glass would not devitrify under conditions which produced devitrification in the non-nuclear-waste-containing glass, exhibited hydrolysis losses lower by an order of magnitude, had high solvency power for those elemental oxides, exhibited little tendency for internal crystallite formation, and possessed other desirable physical characteristics, all in direct antithesis to the properties of the best prior-known glasses used for this application.

Drawbacks are observed that the invention relates to a method for encapsulation of high level radioactive nuclear waste. This is not related with arsenic disposal method.

Reference may be made to Patent No 2267178C1, wherein a liquid waste is successfully vitrified into a glass system comprising Na_2O : 22.0-26.0; Al_2O_3 : 13.0-28.0; B_2O_3 : 3.0-6.0; P_2O_5 : 38.0-55.0; Li_2O : 0.5-1.0. The waste liquid contains high percentage of aluminum and other radioactive elements. Homogeneous glass was formed during this invention.

- 5 Drawbacks are observed that the invention relates to a method for encapsulation of waste liquid. The waste liquid contains high percentage of aluminum and other radioactive elements. This is not related with arsenic disposal method.

- Reference may be made to Patent No US5434333A, wherein a suitable a method for treating materials such as wastes for solidification to form a solid, substantially non leachable product is presented. Addition of reactive silica rather than ordinary silica to the material when bringing the initial molar ratio of its silica constituent to a desired ratio within a preselected range increases the solubility and retention of the materials in the solidified matrix. Materials include hazardous, radioactive, mixed, and heavy metal species. Amounts of other constituents of the material, in addition to its silica content are also added so that the molar ratio of each of these constituents is within the preselected ranges for the final solidified product. The mixture is then solidified by cement solidification or vitrification. The method can be used to treat a variety of wastes, including but not limited to spent filter aids from waste water treatment, waste sludges, combinations of spent filter aids and waste sludges, combinations of supernate and waste sludges, incinerator ash, incinerator offgas blowdown, combinations of incinerator ash and off gas blowdown, cementitious wastes and contaminated soils.

- Drawbacks are observed that the invention discloses a suitable a method for treating materials such as wastes for solidification to form a solid, substantially non-leachable product. Materials include hazardous, radioactive, mixed, and heavy metal species. This is not related with arsenic disposal method. Development of glass products is not revealed.

- Reference may be made to Patent RU2203512C2, wherein a device is invented for immobilizing liquid radioactive wastes. Steps for immobilizing liquid radioactive wastes and details of component are disclosed in the prior art. Fluxing agent is introduced to produce phosphate glass blocks in order to immobilize liquid radioactive waste. Liquid radioactive waste is first pre-immobilized and then mixed with fluxing agents and the mixture is melted and poured into tanks,

blocks are made of it. After that melting is made at 1000-1800° C with direct exposure to induction filed at frequency of 0.3-1.8 MHz.

Drawbacks are observed that the invention discloses a device is invented for immobilizing liquid radioactive wastes. This is not related with arsenic disposal method. Development of glass products is not revealed.

Reference may be made to Patent No EP1034149A1, wherein a method for vitrifying industrial waste into ceramic tiles is proposed. Melting of the waste material to form a glass melt and subsequent annealing were performed to obtain solid glass block. Glass particles of 55 to 99 wt.% and 45-1 wt. % first additive, forms the glass powder mixture into tiles by dry pressing. The process includes a devitrifying step where the solid glass product is devitrified prior to the grinding step or the glass particles in the tile are devitrified after the forming step.

Drawbacks are observed that the invention discloses a method for vitrifying industrial waste into ceramic tiles is proposed. This is not related with arsenic disposal method. Development of glass products is not revealed.

Reference may be made to Patent RU2269833C2, wherein recovery of liquid radioactive waste by vitrification of the liquid was reveals. A solution of boron phosphate or phosphate has been used as base glass matrix and a fluxing agent (sodium tetraborate, sodium hydroxide) is introduced. Fluxing reagent as a form of two solutions is dosed to furnace separately from radioactive wastes without their premixing with wastes.

Drawbacks are observed that the invention reveals recovery of liquid radioactive waste by vitrification of the liquid. This is not related with arsenic disposal method.

Reference may be made to Patent US20160141060A1, wherein a system/ method for vitrification of waste to prevent the formation of molybdate secondary phases has been proposed. The glass forming batch contains a source of vanadium, at least one glass frit, glass flakes or a glass forming oxides. These are fed to the melter. The glass contains 10% vanadium oxide. High level radioactive waste material from activities like weapons programs, nuclear fuel recycling and medical isotope production are being converted to a vitrified product by addition of additives (vanadium).

Drawbacks are observed that the invention reveals a system/ method for vitrification of waste to prevent the formation of molybdate secondary phases. This is not related with arsenic disposal method.

- 5 Reference may be made to Journal “Vitrification and Devitrification of Chromium Containing Tannery Ash (World Academy of Science, Engineering and Technology International Journal of Environmental and Ecological Engineering, Savvas Varitis *et al*, 2015)” wherein high quantities chromium containing tannery ash was incorporated into silica glass and thereafter by thermal treatment glass-ceramics were produced. Tannery wastes were first incinerated at 500 °C in order
10 to reduce the organic contents and chromium was retained at its trivalent state. Thereafter glass forming agents SiO₂, modifiers like Na₂O, CaO was introduced with the waste mix and the mixtures were melted at 1400-1500° C in a resistive heating furnace. XRD, SEM, TEM, DTA etc. different analysis method was done to confirm the state chromium and the glass.

- Drawbacks are observed that the invention discloses a suitable a method for Vitrification and
15 Devitrification of Chromium Containing Tannery Ash. This is not related with arsenic disposal method. Development of glass products is not revealed.

- Reference may be made to Journal ‘Industrial waste derived biosorbent for toxic metal remediation: Mechanism studies and spent biosorbent management’ (Lata Ramrakhiani *et al*.
20 Chemical Engineering Journal 308 2017 1048–1064) wherein the dried activated tannery industry sludge was used as complex biosorbent for removal of Ni(II), Co(II), Zn(II) and Cd(II) in single and multi-component system. The mechanism for toxic metals biosorption was analyzed along with equilibrium isotherm and kinetic study. The efficiency of the biosorbent was studied for real effluent treatment. Zn(II) and Cd(II) showed 99% removal within 10 min while Ni(II)
25 and Co(II) attained 98% removal at 20–24 h. The biosorbent showed >96% removal efficiency for these metals in effluents from battery manufacturing industry with simultaneous removal of Pb, Cu and Fe ions. Chemical modification of hydroxyl, carboxyl, amino, phosphate, sulfonyl and carbonyl functional groups were undertaken and surface characterization of the biosorbent was done using zeta-potential, FTIR, FESEM-EDX and XPS technique to elucidate the
30 biosorption mechanism. Further, safe disposal of the spent biosorbent in glass form was established which is significant for commercial implementation of the biosorption technology.

Upto 30% of metal laden biosorbent could be inertized in phosphate glass matrix as confirmed by the XRD-analysis. No leaching of heavy metals was observed on the glass with thermal cycle at 75 °C for 8 h/day up to 35 days.

- 5 Drawbacks are observed that the invention in prior art literature discloses utilization of dried activated tannery industry sludge for removal of Ni(II), Co(II), Zn(II) and Cd(II) in single and multi-component system. The prior art does not reveals any use of glass produced. Investigation of optical property has not been presented.
- 10 Reference may be made to Patent FR2726492B1, wherein an additive is claimed for stabilisation of aq. sludges produced during metal-rich waste treatment and consisting of pptd. metal cpds. (esp. insoluble sulphides of hydroxides) in aq. phase, especially those obtained from secondary ash from vitrification of domestic waste incineration waste gas cleaning residues. The additive comprises at least 50 wt.% oil-fired power station ash and balance alkaline (e.g. calcium)oxide
- 15 or hydroxide. The treatment process involves: (a) furnace melting of the waste to be vitrified; (b) oxidn. of the furnace off-gas with air at ambient temp.; (c) dry quenching of the oxidised off-gas by dilution with air; (d) filtering; (e) scrubbing to neutralise the off-gas before discharge; (f) recovery of the metal salt-contg. secondary ash produced during steps (c) and (d); (g) formation of an aq. soln. from the secondary ash and pptn. of the metals as insoluble sulphides or hydroxides
- 20 to obtain a sludge and an aq. saline liquor; (h) mixing the sludge with the above additive to stabilise the pptd. metals; (i) withdrawing the supernatant saline liquor; and (j) recovery, by decantation of the sludge, of the insoluble metal salts and the stabilised pptd. metals.

Drawbacks are observed that the invention is not related to the encapsulation of arsenic rich waste in glass making.

- 25 Present invention deals with the incorporation of As contaminated sludge [ACS] obtained from water filtration, into glass to develop heat absorbing properties. The glass composition is optimized incorporating waste sludge in order to reduce NIR (near Infrared) transmission (1000 nm).

- 30 Thus, arsenic contaminated sludge can be trapped into the glass which has high heat shielding properties. This glass has a potential application in optical devices where heat needs to be

shielded. The potential use of this glass can be in window panel significantly reducing air-conditioning load in the building. Further, this glass can of use in glare cutting application.

OBJECTIVES OF THE INVENTION

The main object of the present invention is to provide a method for safe disposal of arsenic rich sludge obtained from treatment of contaminated groundwater and its utilization in developing heat protective glass.

Another object of the present invention is to provide a method of incorporating As containing hazardous sludge into glass matrix without polluting ground water, land or environment.

Yet another object of the present invention is to provide a method of obtaining heat protective property (1000-1100 nm) in glass incorporating As containing sludge (within 10 wt.%) into it.

Yet another object of the present invention is to provide a method of obtaining brown/ black colour in glass incorporating As contaminated sludge into it.

Yet another object of the present invention is to provide a method of incorporating sludge with As to produce glass of practical uses such as decorative glasses, ash tray, table glassware etc.

Yet another object of the present invention is to ensure minimum leaching of toxic element from the glass prepared utilizing As contaminated sludge.

Still another object of the present invention is to develop glass article encapsulating ACS up to 15 wt %.

Yet another object of the present invention is to load maximum ACS up to 40 % into the glass.

Yet another object of the present invention is to develop glass with low visible transmission property and the glass can further reduce IR wavelength causing reduction in heat load.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows photograph of a polished glass pieces of diemension 10 x15 x12 (in mm) prepared incorporating 5-20 % ACS. The glass is brown in colour and darkness increases with increasing ACS loading in it. Figure 1a shows glass prepared with 5% ACS, b. Glass with 10% ACS; c. Glass with 15% ACS; d. Glass with 20% ACS. Brown colour in glass mainly due to iron oxide present in arsenic rich sludge.

Figure 2 represents XRD profile of alumio-zinc-phosphate glass containing 5-20 wt.% of As contaminated solid waste. The figure shows all the sample are amorphous in nature.

Figure 3 illustrate UV-Vis-NIR transmittance spectra of glass containing 5-20 wt.% of As contaminated solid waste. Transmittance above 70 % is seen in the visible region in glass with 5% ACS and less than 40 % at ~ 1000 nm wavelength. Transmittance falls at visible region with higher incorporation of ACS in glass. Visible transmission remains within ~18% while IR transmission is completely blocked. The glass does not show any visible transmission and hence no decorative glass article can be developed with the glass melted incorporating ≥ 20 % ACS loading.

Figure 4 depict UV-Vis spectra of glass prepared with 5% ACS before and after leaching study. Transmittance remains same after leaching investigation of the glass in submerged water for 14 days at 75°C. Inset shows polished glass with 5 % ACS (A) and glass with 5% ACS after leaching study. Both the appears to be identical visually.

SUMMARY OF THE INVENTION

Accordingly, the present invention provides a method for safe disposal of arsenic rich sludge obtained from treatment of contaminated groundwater and its utilization in developing heat protective glass comprising the steps of:

- i. mixing raw material of glass system with 1 to 40 wt. % arsenic containing sludge [ACS] to obtain a mixed batch;
- ii. Sintering the mixture as obtained in step (i) at temperature in the range of 250 to 300 °C for a period in the range of 1 to 2 h to obtained sintered batch;
- iii. melting the batch as obtained in step (i) or step (ii) at temperature in the range of 1200-1300°C for a period in the range of 30-60 min in air atmosphere in a furnace or in microwave heating to obtain melt;
- iv. casting the melt into a preheated metal plate to obtain hot glass;
- v. annealing the hot glass in a muffle furnace within temperature in the range of 350 - 550 °C for a period in the range of 30 min to 1 h followed by controlled cooling until room temperature to obtained cooled glass;
- vi. cutting, grinding and polishing the cooled glass to obtain polished glass sample.

In an embodiment of the present invention, arsenic containing sludge [ACS] is obtained from treatment and filtration of contaminated groundwater containing major elements Fe, and with minor other element As, Si, Al, P, K etc.

In another embodiment of the present invention, Glass system comprising P_2O_5 in the range of 50-75 wt %; ZnO in the range of 5-30 wt %, Na_2O in the range of 1-10 wt % and Al_2O_3 in the range of 2-10 wt %.

5 In yet another embodiment of the present invention, the source of P_2O_5 and Al_2O_3 is Aluminum meta- Phosphate in order to handle less volume of raw material.

In yet another embodiment of the present invention, ZnO is obtained from ZnO or zinc phosphate.

In yet another embodiment of the present invention, Na_2O is obtained from carbonate source (sodium carbonate).

10 In yet another embodiment of the present invention, safe disposal of ACS is ensured by detecting no leaching of toxic heavy metal (As) from the glass after 14 days immersion into distilled water at 75 °C (for 8 h/day).

In yet another embodiment of the present invention, the melting is carried out using quartz, alumina or refractory crucible.

15 In yet another embodiment of the present invention, the melted glass has transmittance up to 40-70 % within wavelength 600-700 nm for 2 mm glass with waste incorporation 5-10 wt.%.

In yet another embodiment of the present invention, the melted glass has transmittance >70 % within 650-700 nm for 2 mm sample thickness for 5 % incorporation of ACS.

In yet another embodiment of the present invention, IR transmission (~1000 nm) <40 % at for 2 mm thickness for 5 wt. % ACS incorporation.

20 In yet another embodiment of the present invention, IR transmission (~1000 nm) <10 % at for 2 mm thickness for 10 wt. % ACS incorporation.

In yet another embodiment of the present invention, more than 40 wt.% ACS can be incorporated into glass.

25 In yet another embodiment of the present invention, different glass products such as decorative glass, table ware glass, window glass, etc. can be prepared incorporating ACS less than 20 wt. %.

DETAIL DESCRIPTION OF THE INVENTION

30 Present invention provides a method for safe disposal of arsenic rich sludge obtained from treatment of contaminated groundwater and its utilization in developing heat protective glass, which comprises preparation of batch from thoroughly mixed ingredients such as aluminum meta-phosphate, ZnO , [Glass system comprising P_2O_5 - ZnO - Na_2O - Al_2O_3], followed by

incorporation of arsenic containing sludge (obtained from treatment and filtration of contaminated groundwater) containing major elements Fe, and with minor other element As, Si, Al, P, K etc., melting at 1200-1300°C for 30-60 min in air atmosphere in an alumina or quartz crucible, followed by casting the melt in a preheated mould and subsequent annealing the hot glass within 330 - 550°C for 1 h followed by controlled cooling to room temperature, followed by cutting, grinding and polishing to obtain polished glass sample.

Present invention deals with the incorporation of As containing sludge (ACS), obtained from treatment and filtration of contaminated groundwater, into glass matrix and optimization of composition incorporating ACS can produce glass particularly Heat shielding glass. Sludge mainly consist of iron oxide and iron oxide in ferrous state absorbs InfraRed (IR) portion of electromagnetic wavelength of light and thereby causes heat absorbing properties. Thus, glasses with heat absorbing properties can be produced by optimizing glass composition and waste loading into glass matrix.

A zinc phosphate base glass composition has been melted incorporating different percentage (5-20 wt. %) of ACS (up to 20 wt. %) to produce glass. The produced glass shows visible transmission 40- 70% (at 600-700 nm) and IR transmission within 40 – 10% T for 2 mm thick glass with incorporation of 5-10% ACS. Further reduction of IR transmission (<10 % T) can be achieved incorporating 10 wt % of waste in glass. Significant chemical durability has also been observed after 14 days under submerged water maintaining thermal cycle at 75°C for 8 h/day. No leaching of hazardous element (Cr, Cd, Fe, Mn, Cu, Co, Ni, Pb etc) is detected in distilled water from the glass containing 5 - 15 wt.% of ACS by ICP AES. Thus, ACS containing hazardous elements can be trapped into the glass, which has high visible transmitting properties and low IR transmission. This glass has a potential application in devices where IR light needs to be curtailed. Potential use of this glass can be as window glass minimizing energy consumption of air conditioning and lighting load particularly in office building, large community hall, meeting room.

UV-Vis-NIR spectra suggest possibility of 30 % reduction in optical transmission at NIR region than visible region and this indicates feasibility of heat shielding glass preparation due to low transmission at 1050 nm.

Preparation of brown and black color in glasses could be achieved varying waste loading into glass. The invention further deals with the preparation of different glasses of practical uses including brown color glasses, table glass ware, ash tray, paper weight, decorative glass product and others.

- 5 Novelty of the present invention is to demonstrate a new method of utilizing sludge containing toxic heavy metal (As) minimizing environmental pollution and thus, to ensure elimination/reduction of hazard associated in waste disposal methods. The invention further describes a process to utilized As-contaminated sludge in production of glasses for practical purposes such as decorative glass, table glass ware etc. The process ensures no leaching or
10 minimum leaching of toxic metal (As) from the prepared glass even after disposal to the environment. In the process, arsenic can be stabilized into glass matrix and thus, eliminating risk of toxic As contamination while handling disposal into the environment.

Initially arsenic rich sludge is collected after filtration from contaminated ground water. The arsenic contaminated sludge (ACS) is dried in order to use for glass making followed by
15 chemical analysis to select the suitable glass composition. Now, the dried ACS is mixed separately with a suitable batch comprising of different raw materials as required by the properties of glass.

The batch is melted in resistance heating furnace using different crucibles (e.g., alumina, quartz or platinum) within melting temperature of 1300–1550 °C depending on the glass composition
20 and melting parameters. The melting could also be carried out in microwave furnace to tailor the optical properties of glass containing transition metals. The melt is cast into a hot mould of desired shape and subsequently transferred into a muffle furnace for annealing the glass followed by controlled cooling up to room temperature. The obtained glass is further processed by cutting, grinding and polishing. Usually small glass pieces of different dimension are prepared for
25 property characterization. Molten glass is placed in shape mold to develop colour glass articles. Arsenic containing sludge is also incorporated into glass matrix, and brown colour glass is obtained. The potential use of this glass is in window panel significantly reduces electricity load in the building.

Steps of glass preparation

- 30 **Step 1-** Mixing of raw materials incorporating As containing sludge (ACS) with different proportion ranging from 1 to 40 wt. %.

- Step 2 -** Sintering the mixed batch at 300 °C for 2 h.
- Step 3 -** Melting the batch (either sintered or as prepared) in resistance heating furnace and or in microwave heating at 1200-1300 °C for 30 min to 1 h in air atmosphere.
- Step 4 -** Casting the melt into a preheated metal plate.
- 5 **Step 5 -** Annealing the hot glass in a muffle furnace within 350 - 550 °C for 30 min to 1 h followed by controlled cooling until room temperature.
- Step 6 -** Processing of glass adopting cutting, grinding, polishing to have desired size of glass sample for property evaluation.
- 10 **Step 7 -** Property evaluation such as XRD analysis, UV-Vis absorption Spectroscopy, XPS Spectroscopy and leaching analysis of polished glasses containing different proportion of ACS.
- Step 8 -** Fabrication of glass articles

EXAMPLES

- 15 The following examples are given by way of illustration of the working of the invention in actual practice and therefore should not be construed to limit the scope of the present invention in any way.

EXAMPLE 1

- 20 A glass was melted from batch containing (mol%) 60 - P₂O₅, 5 - Al₂O₃, 10- Na₂O and 25 - ZnO incorporating 5 wt. % of ACS in alumina/quartz/refractory crucible in conventional furnace in air atmosphere at 1200°C for 30 min. The molten glass was poured into preheated mould and subsequently transferred to muffle furnace maintained at 380°C for 1 h for annealing followed by controlled cooling till room temperature (30°C). The obtained glass was found brown in color.
- 25 A sample was cut and polished with 2 mm thick. The transmission of the glass was found 70% within 650 nm and less than 40 % at 1000 nm. No leaching of toxic heavy metal was detected from the glass kept under distilled water 14 days maintaining a thermal cycle of 8h/day at 75 °C.

EXAMPLE- 2

- 30 A glass was melted from batch containing (mol%) 60 - P₂O₅, 5 - Al₂O₃, 10- Na₂O and 25 - ZnO incorporating 10 wt. % of ACS in alumina/quartz/refractory crucible in conventional furnace in

air atmosphere at 1200°C for 30 min. The molten glass was poured into preheated mould and subsequently transferred to muffle furnace maintained at 380°C for 1 h for annealing followed by controlled cooling till room temperature (30 °C). The obtained glass was dark in colour. A sample was cut and polished with 2 mm thick. The transmission of the glass was found 35-40 % within 650-750 nm and 7-8 % at 1000-1100 nm.

EXAMPLE- 3

A glass was melted from batch containing (mol%) 60 - P₂O₅, 5 - Al₂O₃, 10- Na₂O and 25 - ZnO incorporating 15 wt. % of ACS in alumina/quartz/refractory crucible in conventional furnace in air atmosphere at 1300°C for 30 min. The molten glass was poured into preheated mould and subsequently transferred to muffle furnace maintained at 380°C for 1 h for annealing followed by controlled cooling till room temperature (30 °C). The obtained glass was black in colour. A sample was cut and polished with 2 mm thick. The maximum visible transmission remains within 17% (~740nm) and IR transmission ~ 1% (1000 nm). No leaching of toxic heavy metal was detected from the glass kept under distilled water 14 days maintaining a thermal cycle of 8h/day at 75 °C.

EXAMPLE- 4

A glass was melted from batch containing (mol%) 60 - P₂O₅, 5 - Al₂O₃, 10- Na₂O and 25 - ZnO incorporating 20 wt. % of ACS in alumina/quartz/refractory crucible in conventional furnace in air atmosphere at 1300 °C for 30 min. The molten glass was poured into preheated mould and subsequently transferred to muffle furnace maintained at 380°C for 1 h for annealing followed by controlled cooling till room temperature (30 °C). The obtained glass was black and optical transmission could be recorded from 2mm thick sample.

ADVANTAGES OF THE INVENTION

The main advantages of the present invention are:

1. A method of incorporating arsenic contaminated sludge (ACS) to avoid water, soil and environment pollution. The ACS can be entrapped in the glass causing no contamination to the environment. Therefore, safe disposal of ACS is ensured.

2. No detectable leaching of toxic arsenic from the glass after 14 days immersion into distilled water at 75 °C (for 8 h/day).
3. The ACS can be utilized for specific product like heat protective window glass (IR absorbing properties: <40 % Transmission at 1000 nm with 70 %T at 600-700 nm
5 wavelength for 5 wt.% loading into glass). IR transmission can be further minimized to 10 %T with 10wt.% ACS loading into glass.
4. Use of phosphate glass composition was adopted in order to bring down the melting temperature within 1300 °C unlike in silicate matrix of melting temperature more than 1500 °C.
- 10 5. Quartz or alumina crucible can be used to melt this glass instead of using costly noble metal i.e. Platinum crucible.

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We claim

1. A method for safe disposal of arsenic rich sludge obtained from treatment of contaminated groundwater and its utilization in developing heat protective glass comprising the steps of:
 - 5 i. mixing raw material of glass system with 1 to 40 wt. % arsenic containing sludge [ACS] to obtain a mixed batch;
 - ii. Sintering the mixture as obtained in step (i) at temperature in the range of 250 to 300 °C for a period in the range of 1 to 2 h to obtained sintered batch;
 - iii. melting the batch as obtained in step (i) or step (ii) at temperature in the range of
10 1200-1300°C for a period in the range of 30-60 min in air atmosphere in a furnace or in microwave heating to obtain melt;
 - iv. casting the melt into a preheated metal plate to obtain hot glass;
 - v. annealing the hot glass in a muffle furnace within temperature in the range of 350 - 550 °C for a period in the range of 30 min to 1 h followed by controlled cooling
15 until room temperature to obtained cooled glass;
 - vi. cutting, grinding and polishing the cooled glass to obtain polished glass sample.
2. The process as claimed in claim 1, wherein arsenic containing sludge [ACS] is obtained from treatment and filtration of contaminated groundwater containing major elements Fe, and with minor other element As, Si, Al, P, K etc.
- 20 3. The process as claimed in claim 1, wherein Glass system comprising P_2O_5 in the range of 50-75 wt %; ZnO in the range of 5-30 wt %, Na_2O in the range of 1-10 wt % and Al_2O_3 in the range of 2-10 wt %.
4. The process as claimed in claim 3, wherein the source of P_2O_5 and Al_2O_3 is Aluminum meta- Phosphate in order to handle less volume of raw material.
- 25 5. The process as claimed in claim 3, wherein ZnO is obtained from ZnO or zinc phosphate.
6. The process as claimed in claim 3, wherein Na_2O is obtained from carbonate source (sodium carbonate).
7. The process as claimed in claim 1, wherein safe disposal of ACS is ensured by detecting no leaching of toxic heavy metal (As) from the glass after 14 days immersion into distilled
30 water at 75 °C (for 8 h/day).

8. The process as claimed in claim 1, wherein the melting is carried out using quartz, alumina or refractory crucible.
9. The process as claimed in claim 1, wherein the melted glass has transmittance up to 40-70 % within wavelength 600-700 nm for 2 mm glass with waste incorporation 5-10 wt. %.
- 5 10. The process as claimed in claim 1, wherein the melted glass has transmittance >70 % within 650-700 nm for 2 mm sample thickness for 5 % incorporation of ACS.

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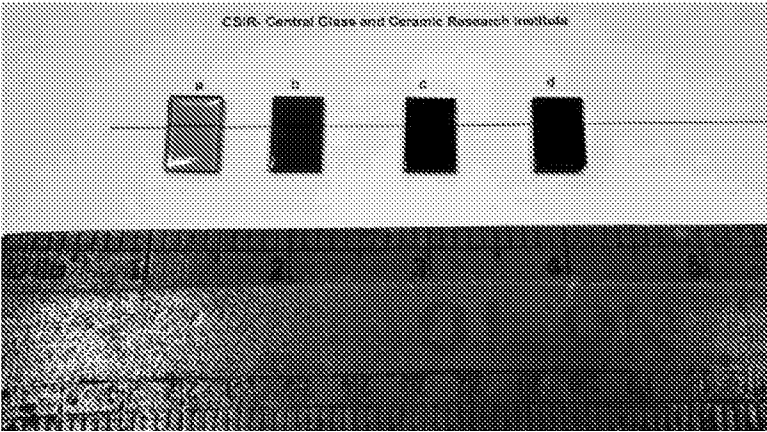


Figure 1

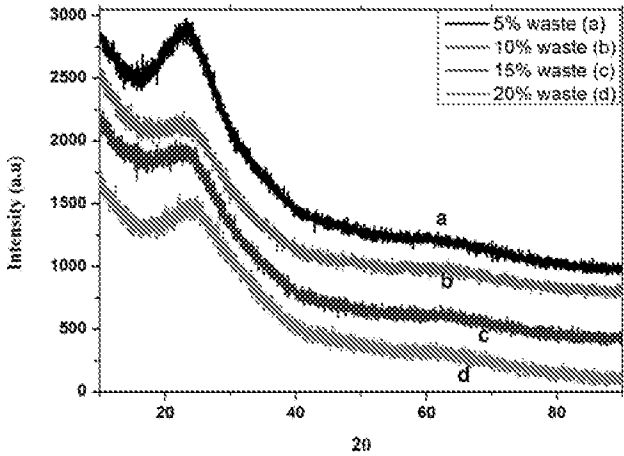


Figure 2

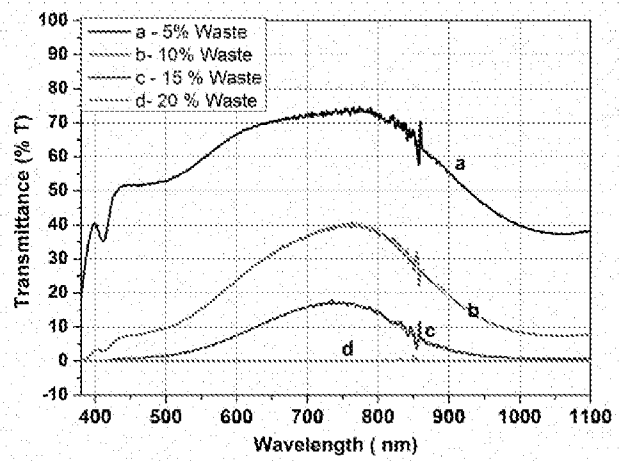


Figure 3

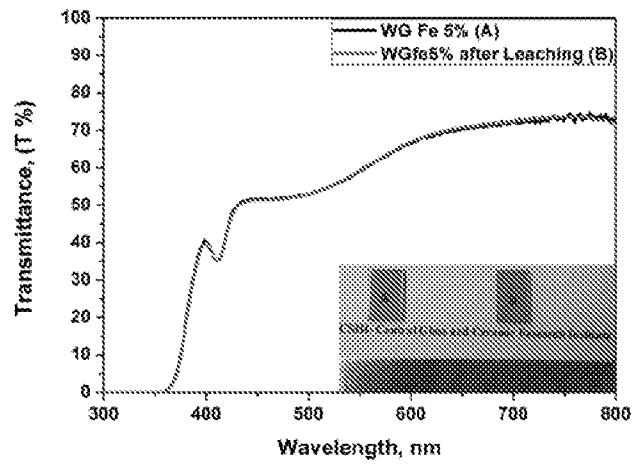


Figure 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IN2021/051196

A. CLASSIFICATION OF SUBJECT MATTER C03C1/00, C03C3/12, C03C3/16, C03C3/17, C03C1/04, C03C4/08, B09B3/00 Version=2022.01 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) C03C1, C03C3, C03C4, B09B3 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) PatSeer, IPO Internal Database		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A, D	EP1946858 (A2) (MARTINEZ MANENT SALVADOR); 23 July 2008 (23.07.2008) paragraph 10	1-10
A, D	CN107311455 (A) (UNIV CENTRAL SOUTH); 03 November 2017 (03.11.2017) abstract	1-10
☐ 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 "D" document cited by the applicant in the international application "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 "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "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 "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 29-03-2022		Date of mailing of the international search report 29-03-2022
Name and mailing address of the ISA/ Indian Patent Office Plot No.32, Sector 14, Dwarka, New Delhi-110075 Facsimile No.		Authorized officer Ch Sree Rama Prasad Telephone No. +91-1125300200