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(73) Proprietor: **WESTINGHOUSE ELECTRIC CORPORATION, Westinghouse Building Gateway Center, Pittsburgh Pennsylvania 15235 (US)**

(72) Inventor: **Greenhalgh, Wilbur Orme, 1950 Jones Road, Richland Washington (US)**

(74) Representative: **van Berlyn, Ronald Gilbert, 23, Centre Heights, London, NW3 6JG (GB)**

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Description

This invention relates to a method of immobilizing nuclear wates. Sodium sulfate radwaste slurry is the prime liquid waste generated from boiling water reactor facilities which use bead resin cleanup. At the present time, the slurry is concentrated into an evaporator to about 25 wt.% and then is immobilized in cement. One drum of slurry generates about three drums of final solidified waste. The solidified waste is shipped to a burial site at a cost that approaches $1000 for the three drums. This situation is considered to be unsatisfactory in the industry due to the high cost involved. Also, to improve the public safety and the industry's image it is desirable to immobilize the waste in a material which has a lower leach rate and a higher mechanical stress than does cement.

While glass is superior to cement as a containment material, until now it has not been possible to immobilize sodium sulfate radwaste in glass material as they are incompatible and tend to form more than one glass phase.

U.S. Patent Specification No. 3 943 062 discloses the solidification of liquid nuclear waste which contains sodium or sodium compounds by calcifying in a fluidized bed.

U.S. Patent Specification No. 4 028 265 discloses a method for converting sodium nitrate containing liquid radioactive waste to a stable form by the addition of clay.

Accordingly, the present invention resides in a method of immobilizing nuclear waste in an aqueous slurry containing sodium sulfate comprising evaporating water from said slurry to produce a concentrate; characterized by mixing into said concentrate from about 50 to 200% by weight based on sodium sulfate weight of a destabilizing compound of a metal which forms an unstable sulfate; and about 5 to about 20% by weight based on the total weight of said sodium sulfate and said destabilizing compound of a reducing agent; heating at from 700 to 900 °C until the evolution of sulfurous gases substantially ceases; mixing with glass formers in an amount of from 65 to 80%, based on total weight; heating to from 1050 to 1200 °C; and cooling to room temperature.

It has, therefore, now been found that sodium sulfate radwaste can be immobilized in glass if it is first treated to remove sulfate. Sulfate removal requires the following two conditions to be present; (1) an unstable (to temperature) sulfate and (2) a reducing atmosphere or matrix. Sodium sulfate of itself meets neither of these conditions as it is a stable sulfate and it is a light oxidizer. The stability of the sulfate is highly dependent on the cation present. While sodium stabilizes the sulfate, it has been found that iron compounds cause instability. Therefore, by adding an iron compound together with a strong reducing agent to sodium sulfate both conditions required for removing sulfate can be met. Once the sulfate has been removed, the remaining radwaste can be combined with glass formers to form a stable glass product.

The compatible glass product generated from a drum of slurry using the process of this invention fills only about a third of a drum rather than the three drums that using cement would generate. As a result of this one-third reduction in waste volume, there is a tremendous savings in transportation and storage cost of the drums. Furthermore, glass immobilized waste has a lower radionuclide leach rate and a higher mechanical strength than does cement immobilized waste. For these reasons the containment of the radionuclides is safer as there is less chance of contamination with the environment.

The process of this invention is applicable to any sodium sulfate containing aqueous slurry. The invention is particularly directed at sodium sulfate slurries containing radioactive waste that are the evaporator bottoms of a boiling water reactor. These slurries are typically about 25% (all percentages herein are by weight) sodium sulfate (based on slurry weight), although in actual practice the sodium sulfate content can vary from 15 to 40%. The slurry may also contain various hydroxide, nitrate, and boric compounds. These compounds are not incompatible with the process of the invention and will aid in making a good quality glass. Certain refractory type elements such as aluminium, zirconium, thorium, and the rare earths, however, should be limited to less than about 5% of the slurry solids because at higher percentages the melting temperature becomes excessive. Halide compounds, with the possible exception of fluoride, should be avoided in excess of 1 or 2% (based on slurry solids) as they tend to form a second glass phase. However, these compounds are generally excluded from the reactor fluid anyway because of their corrosive nature and stainless steel piping. Phosphate and carbonate compounds may also be present, but they are generally compatible with the vitrification process used in this invention.

In a convenient embodiment of the invention the water in the sodium sulfate slurry is evaporated in a first step to less than 5% (based on the total slurry weight) in a stirrer drier to form solid granules or powder. The removal of water is necessary as the presence of too much moisture could cause foam formation or solids bumping, which means that escaping steam blows the solids out of the reaction vessel. The evaporation of the water can be accomplished by heating the slurry to 150 °C for as long as is necessary.

In the next step, a destabilizing compound and a reducing agent are added to remove the sulfate. The addition of a destabilizing compound and the reducing agent may be made prior to evaporation if desired. The reason that sulfate must be removed when sodium is present is that sodium sulfate must be removed when sodium is present is that sodium sulfate melts without decomposing at temperatures near 880 °C and the resulting liquid is non-miscible with a typical glass melt. Glass immobilization of radioactive waste requires the radionuclides and waste to be miscible with glass, and this can only occur after the sulfate fraction is removed. In the process of this invention this is accomplished by causing the formation of sulfates which are less stable than sodium sulfate, followed by the decomposition of the unstable sulfate to various sulfurous gases. This is accomplished by the addition of cations that introduce instability (along with a reducing agent).

The destabilizing compound is a salt of a metal which forms an unstable sulfate. An unstable sulfate is one which decomposes upon heating instead of exhibiting a melting point phase change. Unstable sulfates generally decompose in the 400 to 800 °C range. Suitable destabilizing compounds include ferrous ammonium sulfate, ferrous sulfate, bismuth sulfate, cupric sulfate, aluminium sulfate, gallium sulfate, and manganese sulfate. Ferric compounds, such as ferric sulfate and ferric nitrate, can also be used if a reducing agent in an amount of about 15 to about 20% is added to reduce the ferric compound in place to the corresponding ferrous compound. Particularly preferred is ferrous ammonium sulfate which has been found to work quite well. The amount of destabilizing compounds should be from 50 to 200% of the weight of the sodium sulfate in the slurry. If less than 50% is used, all of the sulfate ion may not be destroyed. More than 200% serves no useful purpose and will simply add to the amount of waste that must be disposed of. Ferric ammonium sulfate is preferably added on a one-to-one weight ratio with sodium sulfate, and graphite is added at about 10% of the total solids weight.

The reducing agent used should be at least as strong a reducing agent as hydrogen (Temp 400 °C). Suitable reducing agents include high temperature hydrogen, dry ammonia, hydrazine, and some light hydrocarbon type amines such as methylamine, dimethylamine and trimethylamine. The preferred reducing agent is carbon, especially in the form of graphite, as it has been found to work well, it is safe to use, and it reacts to produce carbon dioxide which is discharged and eliminated and, therefore, has no negative effects upon the glass product. The amount of reducing agent should be from 5 to 20% based on the total weight of the sodium sulfate and the destabilizing compound. If less reducing agent is used, some of the sulfate may not be decomposed and if more is used, the glass vitrification temperature may be raised.

A suitable composition is from 20 to about 35% based on total composition weight, of a nuclear waste concentrate containing from 15 to 40% sodium sulfate and less than about 5% water, from 50 to 200%, based on sodium sulfate weight, of the destabilizing compound, and from 5 to 20%, based on sodium sulfate plus destabilizing compound weight, of the reducing agent.

In the next step, the slurry concentrate is heated at from 700 to 900 °C to decompose the sulfate to sulfurous gases mainly, sulfur oxide gases such as sulfur dioxide, and to force these gases out of the powder or granular solids. Heating should continue until the evolution of the sulfurous gases substantially ceases, which should not exceed eight hours.

In the next step, the remaining concentrate is mixed with glass formers. Glass formers are compounds routinely used to form glass such as boron oxide, and silica mixed with a glass stabilizer such as alumina or lime. Several combinations of glass formers are suitable in this invention, and they may be selected according to the type of glass that is desired, as is well known in the art. A suitable range for a borosilicate glass composition is from 15 to 40% silica, from 20 to 40% boron trioxide, and from 1 to 5% lime or alumina (to act as a stabilizer by preventing the glass from fracturing after vitrification during cooling), and from 20 to 35% of the waste. If more waste is mixed in with the glass formers, they will not dissolve at the melting temperature and a uniform product will not be obtained. If less waste is mixed in, the amount of waste glass that must be stored will be unnecessarily large. A borosilicate glass consisting of about 33% boron trioxide, about 31% silica, and about 2% alumina or lime, mixed with about 33% of the waste concentrate is preferred.

No clay or cryolite additives are necessary. Halide salts should be avoided because they are difficult to remove and cause the formation of a second phase in the glass melt.

Once the glass formers have been added, the mixture is heated to the melting temperature of the glass, which is typically from 1050 to 1200 °C. Below 1050 °C a homogeneous glass melt may not be achieved, and therefore a poor quality glass or ceramic may result. Higher glass melting temperatures could be used if suitable containers can be found. This temperature is maintained until a homogeneous glass melt is obtained. Generally, about two hours are required to produce a homogeneous product; shorter melting times may result in an inhomogeneous glass melt and therefore a poor product. Longer vitrification times, up to eight hours, are acceptable and are limited only by economics and the corrosion of the container. The melt should be annealed by allowing it to cool gradually to room temperature. This can be done either in the furnace itself or the melt can be poured into containers which are insulated so that the melt cools slowly. For a 6" diameter, 30" deep stainless steel can of glass a minimum annealing time of 4 hours is typical and a maximum annealing time would be 24 hours. The cold glass can then be packaged in drums, or etc. and be transported to storage facilities.

The invention will now be illustrated by the following Examples:

Example 1

A sodium sulfate slurry made of 10 grams of sodium sulfate and 30 grams of water was mixed with 10 grams of ferrous ammonium sulfate and 4 grams of graphite. The mixture was dried by heating at least 150 °C under a partial vacuum for 2 hours to a moisture content of less than 5%. It was then heated to about 800 °C and allowed to react for 4 hours which decomposed the sulfates and drove off the sulfurous gases. The resulting calcine was cooled and 5 grams of it was mixed with 5 grams of silica, 5 grams of boron trioxide, plus a trace of lime stabilizer. The mix was vitrified by melting at 1100 °C until a homogeneous melt was achieved, which required over an hour. The resulting product was a good quality black glass.

Example 2

A slurry containing 80 grams of sodium sulfate and 210 grams of water was mixed with 100 grams of ferrous ammonium sulfate and 40 grams of graphite and was treated as in Example 1 except the sulfate removal time was 2 hours instead of 4 hours. To ten grams of the calcine mix was added 10 grams of silica, 10 grams of boron trioxide, and a gram of lime. This mix was vitrified at 1100 °C to form a good quality glass product.

Other experiments using an iron additive for promoting instability in the sodium sulfate were generally successful. The iron additive used was ferric oxide. However, the use of other sulfates or reducing agents such as zinc sulfate, urea, and carbon without any iron compound being present, were not successful.

Claims

1. A method of immobilizing nuclear waste in an aqueous slurry containing sodium sulfate comprising evaporating water from said slurry to produce a concentrate; characterised by mixing into said concentrate from about 50 to 200% by weight based on sodium sulfate weight of a destabilizing compound of a metal which forms an unstable sulfate; and about 5 to about 20% by weight based on the total weight of said sodium sulfate and said destabilizing compound of a reducing agent; heating at from 700 to 900 °C until the evolution of sulfurous gases substantially ceases; mixing with glass formers in an amount of from 65 to 80%, based on total weight; heating to from 1050 to 1200 °C; and cooling to room temperature.

2. A method according to claim 1, characterized in that the destabilizing compound and the reducing compound are mixed into the slurry prior to evaporation of water from the latter.

3. A method according to claim 1 or 2, characterized in that the water in the slurry is evaporated to less than 5% by weight of the dry solids weight.

4. A method according to claim 1, 2 or 3, characterized in that the concentrate is from 15 to 40% by weight sodium sulfate.

5. A method according to claim 1, 2, 3 or 4, characterized in that the destabilizing compound is ferrous ammonium sulfate, ferrous sulfate, ferric sulfate, ferric nitrate, bismuth sulfate, cupric sulfate, aluminium sulfate, gallium sulfate, manganese sulfate or mixtures thereof.

6. A method according to claim 1, 2, 3 or 4 characterized in that the reducing agent is carbon, hydrogen, dry ammonia, hydrazine, or light hydrocarbon amines.

Patentansprüche

1. Ein Verfahren zur Immobilisierung von nuklearem Abfall in einer wässrigen Aufschlämmung, die Natrium-Sulfat enthält, bestehend aus Verdampfen von Wasser von der Aufschlämmung zur Erzeugung eines Konzentrats; gekennzeichnet durch Einmischen von etwa 50 bis 200 Gew.-%, basierend auf dem Natrium-Sulfat-Gewicht, einer destabilisierenden Verbindung eines Metalls, welches ein unstabiles Sulfat bildet; und von etwa 5 bis etwa 20 Gew.-%, basierend auf dem Gesamtgewicht des Natrium-Sulfats und der destabilisierenden Verbindung, eines reduzierenden Mittels, in das Konzentrat; Erhitzen bei 700 bis 900 °C, bis die Entwicklung von schwefligen Gasen im wesentlichen aufhört; Vermischen mit Glasbildern in einer Menge von 65 bis 80%, basierend auf dem Gesamtgewicht; Erhitzen auf 1050 bis 1200 °C; und Abkühlen auf Raumtemperatur.

2. Ein Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass die destabilisierende Verbindung und die reduzierende Verbindung in die Aufschlämmung eingemischt werden, bevor vom letzteren Wasser verdampft wird.

3. Ein Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, dass das Wasser in der Aufschlämmung auf weniger als 5 Gew.-% des Gewichtes der trockenen Feststoffe verdampft wird.

4. Ein Verfahren nach Anspruch 1, 2 oder 3, dadurch gekennzeichnet, dass das Konzentrat 15 bis 40 Gew.-% Natrium-Sulfat ist.

5. Ein Verfahren nach Anspruch 1, 2, 3 oder 4, dadurch gekennzeichnet, dass die destabilisierende Verbindung Ferro-Ammonium-Sulfat, schwefelsaures Eisenoxydul, schwefelsaures Eisenoxyd, salpetersaures Eisenoxyd, Wismuth-Sulfat, Kupfersulfat, Aluminium-Sulfat, Gallium-Sulfat, Mangan-Sulfat oder Mischungen davon ist.

6. Ein Verfahren nach Anspruch 1, 2, 3 oder 4, dadurch gekennzeichnet, dass das reduzierende Mittel Kohlenstoff, Wasserstoff, trockenes Ammonia, Hydrazin, oder leichte Kohlen-Wasserstoff-Amine ist.

Revendications

1. Procédé pour immobiliser des déchets radioactifs dans une boue aqueuse contenant du sulfate de sodium consistant à évaporer l'eau de la boue pour obtenir un produit concentré, procédé caractérisé en ce qu'il consiste à mélanger au produit concentré, environ 50 à 200% en poids, sur la base du poids de sulfate de sodium, d'un composé métallique de déstabilisation formant un sulfate instable; et environ 5 à 20% en poids, sur la base du poids total de sulfate de sodium et de composé de déstabilisation, d'un agent réducteur; à chauffer à une température comprise entre 100 à 900 °C jusqu'à ce que le dégagement des gaz sulfureux ait complètement cessé; à effectuer le mélange avec des produits de formation de verre en proportion de 65 à 80%, sur la base du poids total; à chauffer à une tempéra-

ture comprise entre 1050 et 1200 °C; et à refroidir à la température ambiante.

2. Procédé selon la revendication 1, caractérisé en ce que le composé de déstabilisation et le composé réducteur sont mélangés à la boue avant d'évaporer l'eau de cette dernière.

3. Procédé selon l'une quelconque des revendications 1 et 2, caractérisé en ce que l'eau contenue dans la boue est évaporée jusqu'à une proportion inférieure à 5% en poids du poids des matières solides sèches.

4. Procédé selon l'une quelconque des revendications 1 à 3, caractérisé en ce que le concentré comprend de 15 à 40% en poids de sulfate de sodium.

5. Procédé selon l'une quelconque des revendications 1 à 4, caractérisé en ce que le composé de déstabilisation est du sulfate d'ammonium ferreux, du sulfate ferreux, du sulfate ferrique, du nitrate ferrique, du sulfate de bismuth, du sulfate de cuivre, du sulfate d'aluminium, du sulfate de gallium, du sulfate de manganèse, ou des mélanges de ces sulfates.

6. Procédé selon l'une quelconque des revendications 1 à 4, caractérisé en ce que l'agent réducteur est du carbone, de l'hydrogène, de l'ammoniaque sèche, de l'hydrazine, ou des amines d'hydrocarbures légères.