Continuous Process for Immobilizing Radionuclides, Including Cesium and Ruthenium Fission Products

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NOTICE

CONTINUOUS PROCESS FOR IMMOBILIZING RADIONUCLIDES, INCLUDING CESIUM AND RUTHENIUM FISSION PRODUCTS

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ABSTRACT

Radionuclide wastes are continuously converted to glass in an electro-heated furnace. The process incorporates an exothermic reaction using silicon or aluminum to form aluminosilicates of low-melt viscosity and high-product durability. The reducing conditions in the melt prevent loss of ruthenium, and cesium is captured in an aluminosilicate lattice.

CONTINUOUS PROCESS FOR IMMOBILIZING RADIONUCLIDES, INCLUDING CESIUM AND RUTHENIUM FISSION PRODUCTS

Research regarding advanced waste product forms for Hanford wastes is centering on two processes: the Aqueous Silicate process which yields synthetic aluminosilicate minerals of the zeolitic variety such as cancrinite; and High-Temperature Melt processes in which molten silicates provide the necessary ion mobility which enables an ionic and molecular cage to be formed for tailoring waste product composition, mineral analogs, and crystallinity of the product. Numerous studies have been conducted using batch-type reactions, but only a few studies have been made on continuous processes. There is need for a continuous process to immobilize approximately 250,000 tons of Hanford wastes.

The Atlantic Richfield Hanford Company work as described in this paper is covered by United States Patent No. 3,849,330. The process comprises an overall continuous process for immobilizing radionuclides in complex aluminosilicates. Cesium, strontium, ruthenium, and the actinides are cations that may require special consideration in ultimate disposal of radioactive wastes. Strontium and plutonium both have long-lived radioactivity and are bone-seekers in the body, which makes their immobilization especially important. Cesium has a much shorter biological half-life than strontium; but because most of its compounds are highly soluble, cesium also requires special consideration for immobilization. Ruthenium is a metal with some unusual properties. As the tetroxide, it is volatile at 25° C and as ruthenate and perruthenate it is soluble in water. Because of these two characteristics of mobility, it is

given special consideration. Fortunately ruthenium radio-
activity has a half-life of about one year, and after storage
for 20 years the radioactivity is reduced by a factor of
about one million.

Strontium and plutonium both form highly insoluble
silicates but cesium silicate is soluble, being similar to
sodium silicate. However cesium aluminosilicate, pollucite,
has a very low solubility.

Radioactive wastes are generally in the form of
nitrates unless they have been calcined to a solid oxide
product. The problem is to convert these materials to
silicates and/or aluminosilicates in a continuous process to
obtain a product of sufficiently low viscosity to permit
easy casting and of sufficient leach resistance to give good
immobility. Glass-making-type furnaces can be used to
produce a silicate melt incorporating the radionuclides. To
minimize the problem of isolating the radioactivity, the
method of heating should not generate significant flue gas.
Heating is readily controlled by using electrical energy.
For this reason a glass-making-type furnace with induction
heaters would be preferred. Induction heaters are capable
of bringing the melt in the furnace to 1450° C. In one
limit of the source of heat, all the heat would be supplied
electrically and the process might be termed an Endothermic
Silicate Melt process.

To convert ruthenium to the reduced elemental state, a
reducing condition should be maintained in the melt. This
is accomplished by addition of a small percentage of metal
fuel (silicon or aluminum) in the solid feed to the furnace.
This solid feed is in the form of a granular pre-mix com-
posed of the waste in granular form, either as oxide gran-
ules or as dry nitrate salt. Sources of silica and alumina

also are required to convert these wastes to silicates and
aluminosilicates. This may be provided in part by inert
crushed basalt or a selected sand, and in part by the use of
elemental silicon and/or aluminum metal fuel to maintain the
desired reducing conditions by an exothermic, thermite-type
reaction. Different formulations for the pre-mix are needed
for different types of wastes and different sources of
aluminosilicate. In the other limit of the source of heat
for the process, all the heat may be supplied by the exo-
thermic reaction. This amounts to a continuous thermite
process, and is not the preferred mode because control is
more difficult.

The preferred mode of the process is one that involves
supply of 80% or more of the necessary heat by electrical
means and 20% or less by means of the exothermic reaction.
This would provide both maximum control and better economy
than a completely exothermic process. Figure 1 shows a
schematic flowsheet of the preferred process as described in
U. S. Patent 3,849,330. This sketch shows a furnace with a
silicate melt phase in the upper zone and a molten metal
phase in the lower zone. The molten metal phase will be
present only when a sufficient amount of the heat required
is supplied by the exothermic reaction and when iron oxide
is used in the pre-mix as a source of oxygen. When this is
not the case, the melt would consist only of silicates and
aluminosilicates.

Cesium oxide, if not restrained by an aluminosilicate
cage, is volatile at temperatures of a few hundred degrees
Celsius, considerably below the melt temperature of about
1200° C. As a result, when fission-product cesium is in the
form of oxide or cesium nitrate, cesium will tend to vapor-
ize in the gas above the melt. For this reason in the

preferred process the gases and sublimates (including that
of cesium oxide) are removed and condensed in a cooled
cyclone separator. The solid particulates are to be peri-
odically flushed out with water previously used for scrub-
bing stack gases, as indicated in the right of the Figure.
This recycling of small amounts of particulates and vola-
tiles collected in the water from the scrubber, and combi-
nation with the larger particulates collected in the cyclone
separator, is the first step in immobilization of vola-
tilized radioactive cesium by the aqueous silicate process.
The lower center of the flowsheet indicates the Aqueous
Silicate process conducted at atmospheric pressure and a
temperature of 90° to 100° C in a system with a pH of 10 or
more. Sources of silica and alumina are to be added in suf-
ficient quantity to convert cesium hydroxide to cesium
aluminosilicate in the form of pollucite. If a pH less than
10 is used, and if the waste solution contains nitrate,
cancrinite will be formed rather than the more stable, less-
soluble pollucite. Conversion of previously volatilized
cesium to a stable, immobilized pollucite form is an impor-
tant step in the Continuous process. In the Aqueous Sili-
cate process, cesium crystallizes out in microcrystalline
form along with other insoluble silicates and aluminosili-
cates. These fine, crystalline solids are removed from the
liquor by a continuous centrifuge or rotary filter-dryer and
the dry solids recycled to the pre-mix feed for the continu-
ous furnace. The filtrate and wash liquor are recycled to
the aqueous silicate chemical reactor.

If a low viscosity melt is desired, iron silicate
(fayalite) can be used as a significant portion of the inert
feed. The viscosity of a melt of three-dimensional "frame-
work" silicates is lowered by the presence of orthosilicates

such as fayalite. If silicon metal is used as a fuel and
reducing element, iron oxide can be added to the pre-mix as
an oxygen source to produce fayalite by reaction.

Pollucite can be dissolved in the molten silicate glass
in the furnace. Cesium has a much smaller volatility when
added as pollucite rather than as the oxide or nitrate. As
explained in an earlier paper,[1] cesium is associated with a
cage of 12 oxygen atoms from a silicate lattice which traps
the cesium and decreases the volatility even in a molten
aluminosilicate glass. Only after the temperature is raised
above 1400° C does the volatilization of cesium become sig-
nificant once cesium is trapped in the silicate lattice of
an aluminosilicate melt.

There is no question that the Continuous Endothermic
process for melting silicates can be conducted in a glass-
making furnace heated electrically, such as is practiced in
the glass industry. However there has been no continuous
product output for a Thermite process or combinations of the
endothermic and exothermic methods in a Continuous process.
For this reason a continuous exothermic reaction was con-
ducted for a short time using an expendable furnace. The
concept for the continuous exothermic reaction is shown in
Figure 2.

In its simplest form the continuous exothermic process
involves a furnace in the shape of a "U" tube with raw feed
entering the reaction zone side of the U tube and the molten
product overflowing at a lower elevation from the other
side. A low-viscosity melt is required to permit overflow
of the liquid melt before solidification.

[1]R. E. Isaacson and L. E. Brownell, "Ultimate Storage of
Radioactive Wastes in Terrestrial Environments," OECD/NEA,
*IAEA Proceedings, Management of Radioactive Wastes from
Fuel Reprocessing,* Paris, France, November 1972.

To provide more hydraulic head for flow of the molten silicate in the test, the outlet end of the box was buried about 6" lower than the feed end of the box.

The pre-mix for the reaction consisted of three parts:

1. The starter mix required to fill the furnace U tube and to initiate the reaction.

2. The lower intensity feed pre-mix in the form of one-pound balls covered with aluminum foil.

3. The higher intensity feed pre-mix also in the form of one-pound balls covered with aluminum foil.

The lower intensity and higher intensity feed pre-mixes were used to provide a means of control of the reaction rate in addition to the feed rate. Pre-mix quantities were 100 pounds each for the starter, lower intensity feed, and higher intensity feed. The formulations for the pre-mixes are shown in Figures 3 and 4. In the preferred process the fuel is limited to assure that the reaction remains chemically subcritical so as to preclude runaway reactions and possible explosions.

To demonstrate the continuous thermalt reaction, the reaction zone of the buried expendable furnace was first filled with the 100 pounds of starter pre-mix. The 200 balls of one-pound quantity of feed pre-mix were located at a distance of several feet from the feed end of the furnace. An 8" diameter pipe was used as a guide for the pre-mix balls as they were introduced into the feed side of the furnace after ignition.

The continuous exothermic reaction was initiated by ignition of the starter pre-mix at the feed side of the furnace using as a fuse a commercial thermite starting powder on paper. A few minutes after ignition, the reaction

of the starter pre-mix had proceeded to the bottom of the
U tube. Within five minutes after ignition, the reaction
had proceeded to the outlet end of the furnace and a molten
stream of silicate began to flow from the outlet nozzle. By
this time, five minutes, the reaction rate had subsided
sufficiently to permit the addition of the balls of feed
pre-mix.

The feed pipe was placed in an inclined position between
the supply of feed balls and the feed side of the reaction,
and higher activity pre-mix was added to the feed side to
maintain the rate of reaction. Feeding was performed inter-
mittently with removal of the pipe between feeding sequences
to prevent meltdown of the pipe. This maintained the flow
of molten silicate product from the outlet side of the
reactor, and the melt was collected in a container below the
outlet nozzle, as shown in the photograph in Figure 5. Dur-
ing feeding, the insulation on the top of the stack on the
feed side was broken away from the furnace to permit easier
access to the reaction zone. Figure 6 is a photograph of
the feed side of the furnace showing the hot reaction zone,
feed pipe, broken stack of the feed side, and intact stack
of the outlet side.

Feeding was continued intermittently for the next 30
minutes, switching from higher activity to lower activity
feed. The lower activity balls of feed tended to produce
some red fumes of nitrogen oxides and were not considered as
satisfactory as the higher activity balls of feed. The
reaction could be maintained using either of the feed pre-
mixes.

The outlet opening was exposed to cooling and was
rather small (about 2 inches in diameter). It built up
slowly with silicate solidifying from the melt flowing out

of the reactor. Feeding was continued, and addition of the
200 balls of one-pound weight was completed 35 minutes after
ignition.

The formulations for the starter pre-mix and both the
feed pre-mixes were high in iron oxide and silicon so as to
favor the formation of a low-viscosity fayalite glass. True
to expectations, the product had a very low viscosity and
flowed readily as a thin stream from the outlet spout to the
container below. Maximum flow rate occurred at the end of
the reaction after the insulation had been removed from the
outlet side. The hot melt then flowed as a stream a few
inches wide at a linear rate of several feet per minute.
The visual estimate of viscosity based on previous observa-
tions of flow of viscous fluids was in the range of a few
poises. This material would be easy to pour and cast.

The container below the discharge spout held about 200
pounds of product. After removal of the product from the
container, a layer of metal about 2 inches thick was found
at the very bottom. Above this was a dense layer about
10 inches or more thick of very dark-green (nearly black)
glass which was essentially free of metal particles. At the
top there was a thinner layer, about 4 to 6 inches thick, of
dark glass with more porosity and some vesicular voids.
This top layer also contained some metal globules. A 4- to
5-inch diameter hole existed from the top surface down to a
depth of about 8 inches, possibly caused by escaping gases
and/or shrinkage as the container of molten silicate solidi-
fied. The center of the product was quite dense, black,
with some striations and produced very sharp edges when
fractured.

Prior to the demonstration of the continuous thermite
reaction #E-18, three previous reactions, E-15 through E-17,

were conducted and provided information on the separation of
the metal phase from the silicate phase in the thermite-type
reaction. The formulation of the pre-mix is an important
factor in determining whether or not a reduced metal phase
would be produced--and if produced, whether or not the metal
phase would separate easily from the silicate phase. In
general, iron silicate is beneficial in the product as it
lowers the viscosity and melting point. Use of aluminum
metal as a fuel in the thermite reaction produces strong
reducing conditions and tends to reduce iron silicate to
elemental iron. If the beneficial influence of iron sili-
cate is to be retained, the use of silicon metal as the fuel
is preferred, at least in part. Iron oxide is used with the
silicon metal as a supplemental source of oxygen and if
present in the pre-mix formulation at 40 wt% or more, an
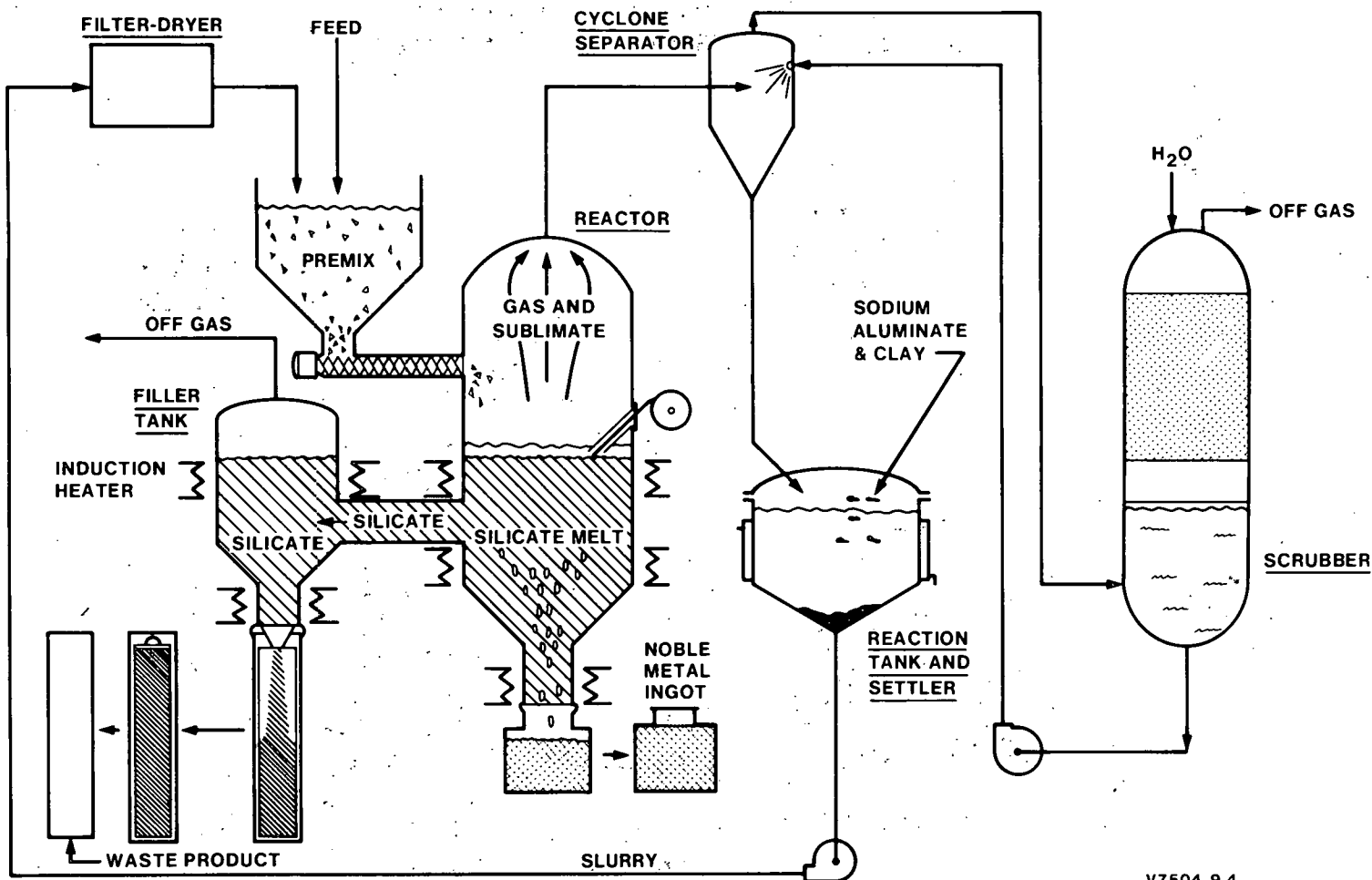easily separated metal phase is formed.

Samples of the silicate phase from the product of E-15
were tested for melting point and for leach rate. The
samples softened at 900° C and partially melted at 1100° C
and became completely fluid at 1250° C. The leach rates
after 96 hours of leaching were 1.24×10^{-6} g/cm^2 d bulk,
4.6×10^{-8} g/cm^2 d for Sr, and 5.0×10^{-9} g/cm^2 d for Cs.
The strontium and cesium cation concentrations in the pre-
mix were approximately 1 wt%.

In batch thermite reaction number E-17 the weight
percentage of iron oxide was increased to 41.67% with a
reduction in the simulated salt cake, trace element, and
sand percentages. The reaction of number E-17 was rapid and
lasted for 13 minutes. The product consisted of two well-
separated distinct phases. The top portion was a dense grey
glass with some small vesicular pores about 1/32 inch in
diameter. A metal regulus about 1 inch thick and 8 inches

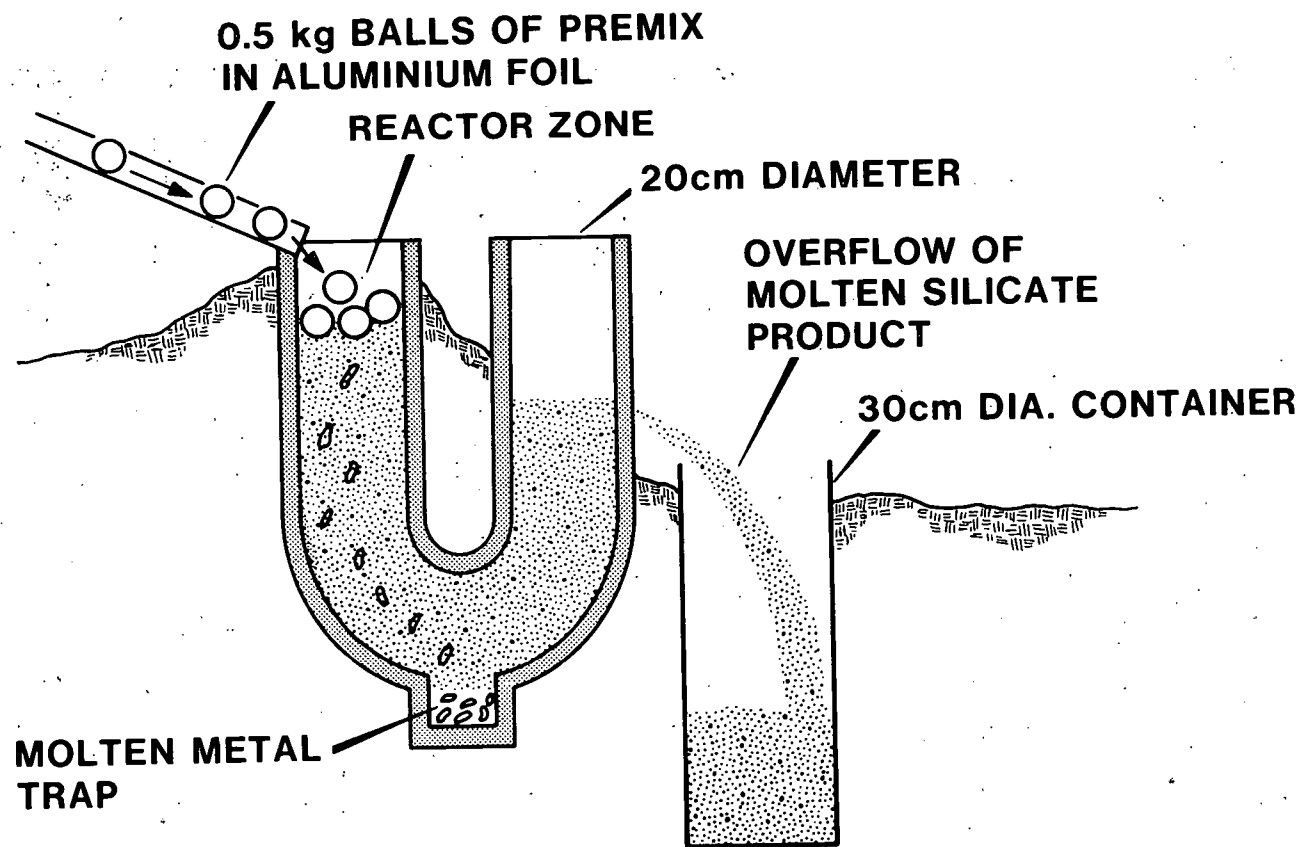in diameter was at the bottom below the silicate phase.

Samples of the metal regulus from reaction number E-17 were dissolved in acid and analyzed for cation by atomic absorption. Note may be made that there was no cesium, strontium, or rare earth cations detected in the metal phase. Previous analysis of products by ARHCO's Chemical Technology Laboratory with similar pre-mix formulations have also indicated that these cations are found only in the silicate phase. The metal regulus was approximately 80% iron with considerable silicon. Hydrofluoric acid was used for dissolution, and some silicon was lost during analysis, therefore silicon was not reported. Both cobalt and nickel were found in the metal phase in nearly the same quantities as present in the pre-mix, indicating very good extraction of these metals by the metal regulus. If noble-metal, fission-product cations such as Ru, Rh, and Pd were present, they would be expected to follow the same path as Ni and Co.

More work is required to evaluate a variety of compositions for tailoring product characteristics and for incorporating the off-gas scrubbers and feedback concepts; however the preliminary findings have been encouraging and indicate that a Continuous process is feasible.

FIGURE 1

CONTINUOUS SILICIFICATION OF RADIOACTIVE WASTES

V7504-9.4

ARH-SA-222

11

0.5 kg BALLS OF PREMIX
IN ALUMINIUM FOIL

REACTOR ZONE

20cm DIAMETER

OVERFLOW OF
MOLTEN SILICATE
PRODUCT

30cm DIA. CONTAINER

MOLTEN METAL
TRAP

V7504-9.3

FIGURE 2

CONTINUOUS EXOTHERMIC PIPE REACTOR

MAJOR COMPONENTS	WT%
$NaNO_3$	8.33
$NaAlO_2$	2.78
Na_2CO_3	2.22
$NaNO_2$	2.22
Fe_2O_3 (RED)	41.67
SOIL (SANDY HANFORD)	11.11
Si METAL	15.00
TRACE ELEMENTS AS NITRATES, PLUS ADDED Si and SAND	16.67
TOTAL	100.00

V7504-9.1

FIGURE 3

THERMALT #E-18 STARTING PRE-MIX FORMULATION

	LBS
Ai FOIL (100 PIECES)	
$NaNO^3$	25.0
Na_2CO_3	2.5
Fe_2O_3 (RED)	40.0
Si METAL	20.0
SOIL (SANDY HANFORD)	12.5
TOTAL	100.0

V7504-9.2

FIGURE 4

THERMALT #E-18 - FEED PREMIX

FIGURE 5

MOLTEN SILICATE FLOWING INTO CONTAINER

FIGURE 6

THE REACTION ZONE AND OUTLET SIDE STACK DURING REACTION