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Report On
PREPARATION OF RADIATION SOURCES
FROM FISSION PRODUCTS BY THE CLAY PROCESS

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ABSTRACT

This study was made to determine the feasibility of producing usable radiation sources by the montmorillonite clay process. The clay process was developed at Brookhaven National Laboratory primarily to solve the problem of ultimately disposing of waste fission products. After reviewing the process in detail, it is shown that radiation sources may be prepared with specific activity as high as 4.5 curies of cesium-137 per gram of clay. Sources of this strength would be entirely suitable for such processing applications as promotion of chemical reactions, preservation of foods, or sterilization of drugs. Furthermore, the operations involved in the clay process are simpler and more straightforward than those of any other process for making radiation sources from fission products. It is concluded from this study that some clay sources should be prepared to demonstrate the actual process.

INTRODUCTION

The future of atomic energy as a primary source of power is becoming brighter with more power reactors being planned or constructed. With the growth of an atomic power industry will come an associated growth of chemical plants devoted to the reprocessing of spent reactor fuel elements. One of the more serious problems to be encountered by these reprocessing plants is the storage and disposition of the radioactive fission products which are separated from the unburnt fuel. The disposal of the so-called waste fission products has been the subject of several research programs during the past few years.

As the number of curies of fission products produced per year increases, the concept of utilizing these wastes as radiation sources becomes increasingly attractive. The construction at Oak Ridge National Laboratory of a multimillion dollar pilot plant for the production of Cs^{137}Cl is evidence of this trend in thinking. This study has been undertaken along similar lines of reasoning to determine the feasibility of preparing a usable, safe, and relatively inexpensive source of radiation from fission products by a process different from that employed at Oak Ridge. The process considered is basically that of adsorbing Cs^{137} on montmorillonite clay.

This report contains a brief discussion of the principles of the clay process and a description of the type of source produced. A proposed laboratory procedure for preparation of a small source is included. Conclusions regarding the

advantages and disadvantages of the clay process based on the findings of this study are given. Appended to the report are complete and detailed calculations on which the conclusions are based.

PRINCIPLES OF THE CLAY PROCESS

The essential principles underlying the clay process are taken from a series of studies made at Brookhaven National Laboratory (3,4,7). The fundamental paper of this series (7) is concerned with the adsorption phenomenon of montmorillonite clay. This clay possesses the property of being able to adsorb large numbers of cations from extremely dilute solutions through an ion exchange type of mechanism. There appears to be a high degree of selectivity exhibited by the clay for the fission product cations. However, trivalent cations such as Al^{+++} are also quite strongly adsorbed and present difficulty when present as interfering ions in the adsorption of Cs^{137} . It is, therefore, imperative to get as good a separation of Cs^{137} and Al^{+++} as possible for this process, if the ion sites in the clay are to be filled largely with fission product cations.

Another unique property of montmorillonite clay is that it can be ground and mixed with water, and extruded into a "spaghetti-like" material that is ideal as a column packing. The spaghetti-formed clay is a stable aggregation and is physically unaffected by passing through it dilute solutions. Thus, it is a simple operation to remove fission product cations from a dilute solution by running it through a column packed with the spaghetti-formed clay.

The fission product wastes which are considered here for preparation of radiation sources have large amounts of aluminum ion present. The best method of separating out the aluminum for this process appears to be by calcining the waste at high temperature followed by leaching. The calcination converts all the cationic materials to the oxide. The oxide of aluminum is extremely insoluble while those of the fission products do dissolve. The leaching agent which gives the highest ratio of the fission product, Cs^{137} , to Al^{+++} , is distilled water (4). This solution will produce the best radiation source after adsorption of the cesium in clay.

Thus, the calcined wastes are leached with a large volume of distilled water. The dilute leaching solution is then passed through the columns of clay. Here the cations of the fission products, notably Cs^{137} , are removed by ion exchange.

Following adsorption of the cations the clay is fired at $1000^{\circ}C$. This fixes the adsorbed ions in the clay lattice so that they cannot be leached out except by the most drastic means, such as by using strong acids. This makes the clay comparatively safe to handle, for it will not release the radioactive cations. If the clay is used as a radiation source for a while and then disposed of by burying in the ground, one can be sure that the radioactivity will not get away. This is extremely important in considering any ultimate disposal of the fission products.

The principles of the clay process make it adaptable to more uses than preparation of a radiation source. In fact, the process was originally developed as purely a disposal method.

If applied to the treatment of large urban water supplies contaminated by radioactive fallout, the clay process could be used to purify the water. In this study, of course, the emphasis is on preparation of radiation sources.

After the clay is fired and the radioactivity locked in the lattice structure, the radiation source is made by simply packaging the clay in aluminum containers. As will be shown, the specific activity of the clay is such that sources of hundreds and thousands of curies can easily be made. Because of the container walls, it is only the gamma radiation which can penetrate and be used. The beta radiation will be absorbed and will serve simply to heat up the source.

THE MONTMORILLONITE CLAY SOURCE

This study indicates, according to the calculations given in the Appendix, that a gamma radiation source can be prepared with a specific activity as high as 4.5 curies of Cs^{137} per gram of clay and a density of 2.2 grams per cc. A one kilo-curie source of this type will weigh 222 grams and have a volume of approximately 100 cc. This is sufficiently concentrated to make it a useful radiation source for processing applications.

Because of the simplicity of the process, a clay source should be comparatively inexpensive to fabricate. Also the low density of the clay reduces the self absorption of gamma radiation to a small amount.

The safety of a clay source should be emphasized, especially when comparing it with cesium chloride. The chloride is extremely soluble and is therefore especially hazardous if

used near water. The clay source is extremely insoluble and wet conditions are of little concern. The clay source is directly ready for safe disposal when it is no longer useful. This certainly is not the case with cesium chloride. For its ultimate disposal it must either be fixed in clay or it must be perfectly sealed in a corrosion-proof container. A montmorillonite clay radiation source sealed in an aluminum container evidently possesses several advantages. Its biggest disadvantage probably occurs in connection with its specific activity. It is possible to make cesium chloride sources with several times the specific activity of the clay. However, for many processing applications, such high specific activity is not required, so that the clay source should be entirely satisfactory.

PROPOSED LABORATORY PROCEDURE
FOR PREPARATION OF A CLAY SOURCE

This study indicates the worthwhileness of making some small clay sources. Consequently, it is proposed that a sample of the Arco, Idaho, high level waste be solidified and calcined at 550°C in a porcelain crucible. The vapors should be carefully de-entrained to remove all condensables that might contain radioactivity. All gases or vapors should be monitored to determine activity before venting them to the stack. A schematic diagram of this procedure is shown in Figure 1 of the Appendix.

The calcined oxide is to be leached in the same crucible to avoid unnecessary handling. This is accomplished by recirculating the leach water through the crucible containing the oxide from a leach reservoir of a larger volume. A small

jet or other type of sealed pump is used for recirculation. Approximately one month is required to remove the maximum percent of Cs from the oxide (4).

The recirculating lines are so connected (see Figure 2) that the solution, after leaching operation is complete, is jetted from the reservoir to the clay columns. By using several columns in series, decontamination is high so that the exit solution can be run to the sewer. As each column of clay becomes saturated, it is replaced with a fresh column. The solution contacts the fresh column last to give the desired decontamination. Saturation of the clay is easily determined by counters at the inlet and outlet of each column. When the clay in a given column is saturated, the column is drained and fired using an induction furnace (Figure 3).

After firing, a piston, fitting inside of the quartz column wall, forces the "spaghetti" out of the column and into the aluminum tube. The tube is supported in a close-fitting steel case, allowing the clay to be pulverized and compressed in the tube. This supporting case is shifted remotely when the tube is filled and the tube is raised and welded shut. The tube is finally transferred to a lead pig for shipping.

CONCLUSIONS AND RECOMMENDATIONS

It is the primary conclusion of this study that the preparation of powerful fission product radiation sources by the montmorillonite clay process is both possible and desirable. Specific activities up to 4.5 curies of Cs-137 per gram of clay can be obtained. Sources made of the clay are sufficiently

concentrated so that many curies of activity may be assembled in reasonably small volumes for processing applications.

The clay process, which involves calcining, leeching and absorption of the fission products, and firing and packaging of the clay, is comparatively simple and should be operable behind thick shielding. The permanence of clay sources and their readiness for ultimate disposal after use give them advantages not possessed by other sources prepared from fission products.

Because of the feasibility of the clay process, it is recommended that some small sources be prepared in a bench-scale operation. It is believed that most of the operations could be carried out in conventional laboratory equipment. Special devices would be required to prepare the clay and to load and seal the clay in aluminum capsules. Preparation of these small sources would demonstrate the complete workability and simplicity of the process. Following the bench-scale operations larger pilot plant equipment should be constructed to prepare sources that would compete with cobalt-60. When sufficient fission products are available, it might no longer be necessary to use up valuable nuclear reactor time to make cobalt-60 sources, since fission products would serve in their stead. Production of cheap radiation sources is necessary if a radiation processing industry is to be developed. It is doubtful that nuclear reactors can ever be operated to make artificial isotopes, such as cobalt-60, very cheaply. Fission products, being a true waste by-product of the nuclear power industry, have the potential, at least, of being made available at comparatively low cost.

APPENDIX

Calculation of Clay Source Activity

The composition of Arco high-level wastes before evaporation is as follows [for first raffinate (1AR)]. (1)

$$\text{Al}(\text{NO}_3)_3 = 1.58 \text{ M}$$

$$\text{NH}_3 = 0.25 \text{ N}$$

$$\text{F.P. (Fission Products)} = 0.31 \text{ gram/liter}$$

$$\text{SP. GR.} = 1.247$$

After concentrating to 2.2 M $\text{Al}(\text{NO}_3)_3$ before storing (2), the concentration of fission products becomes

$$\frac{2.2}{1.58} \times 0.31 = .0432 \text{ gram/liter}$$

For normal fission products, cooled 100 days, the amount of radioactive cesium-137 is 6.2 % (3), while 6 % of the F.P. is Cs^{135} (11). The total amount of Cs in the waste is

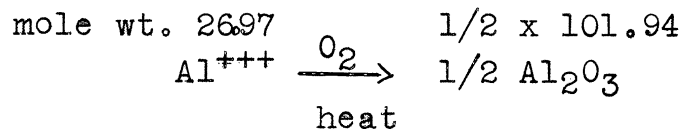
$$.122 \frac{\text{g. Cs}}{\text{g. F.P.}} \times 0.432 \frac{\text{g. F.P.}}{\text{liter}} = 0.0525 \frac{\text{g. Cs}}{\text{liter}}$$

Upon solidifying and calcining the aqueous waste at 550°C, the amount of Cs in the calcined oxides may be determined as follows:

$$\text{Al}(\text{NO}_3)_3 = 2.2 \text{ molar}$$

therefore $\text{Al}^{+++} = 2.2 \text{ molar}$

$$\text{Al}^{+++} = 2.2 \frac{\text{moles}}{\text{liter}} \times 26.97 \frac{\text{gram}}{\text{mole}} = 59.2 \frac{\text{g. Al}^{+++}}{\text{liter}}$$



$$59.2 \text{ grams} \qquad \qquad \qquad \text{x grams}$$

$$59.2 \frac{\text{g. Al}^{+++}}{\text{liter}} \approx 59.2 \times \frac{1/2 \times 101.94}{26.97} = 112 \frac{\text{g. Al}_2\text{O}_3}{\text{liter}}$$

There was also 0.0525 g. Cs /liter, therefore,

.0525 g. Cs in 112 g. Al₂O₃ or

$$\frac{.0525}{112} = 4.7 \times 10^{-4} \frac{\text{g. Cs}}{\text{g. oxides}}$$

Note: In this calculation the oxides were considered to be pure Al₂O₃ since the amount of other oxides adds a negligible amount to the weight of Al₂O₃.

Using distilled H₂O to leach the Cs from the calcined Al₂O₃, the Al⁺⁺⁺ concentration in the leach solution is 10⁻⁵ normal (4). The amount of Cs leached in 25 days is 75 % (5). The concentration of Cs in the leach using 100 cc distilled H₂O per gram of oxides (6) is

$$.75 \times \frac{4.7 \times 10^{-4} \frac{\text{g. Cs}}{100 \text{ cc leach}}}{137 \frac{\text{g}}{\text{mole}}}$$

$$\begin{aligned} \text{Cs conc.} &= 2.58 \times 10^{-6} \frac{\text{mole}}{100 \text{ cc}} \\ &= 2.58 \times 10^{-5} \frac{\text{mole}}{\text{liter}} = M = N \end{aligned}$$

Since both trivalent Al⁺⁺⁺ and Cs are strongly adsorbed by montmorillonite clay by an ion exchange mechanism, it is logical to assume that these ions will be adsorbed in proportion to their concentration in equivalents, or normalities.

The capacity of the clay is 1.12 milliequivalents per gram (7). The amount of Cs adsorbed by the clay is

$$\frac{\text{equivalents of Cs}}{\text{total equivalents (Al + Cs)}} \times \text{capacity}$$

$$\frac{2.58 \times 10^{-5}}{10^{-5} + 2.58 \times 10^{-5}} \times 1.12 = 0.81 \frac{\text{milliequiv. Cs}}{\text{gram clay}}$$

converting milliequivalents to grams

$$.81 \text{ millieq.} = \frac{.81}{1000} \times 137 \frac{\text{gram}}{\text{eq.}} = 0.111 \frac{\text{g. Cs}}{\text{gram clay}}$$

but, only 51 % (11) is Cs¹³⁷

or
$$.51 \times .111 \frac{\text{g. Cs}}{\text{gram clay}} = .057 \frac{\text{g. Cs}^{137}}{\text{gram clay}}$$

Calculating the activity of pure Cs^{137} , $t_H = 33 \text{ yr.}$

$$t_H = .693/\lambda \quad (8)$$

$$\text{activity} = N\lambda \quad (9)$$

where t_H is half life, λ is the decay constant, and N is the number of molecules of Cs^{137} per gram.

$$t_H = (33 \text{ yr.}) (365 \frac{\text{day}}{\text{yr.}}) (86400 \frac{\text{sec.}}{\text{day}})$$

$$= 1.04 \times 10^9 \text{ sec.}$$

$$\lambda = \frac{.693}{t_H} = \frac{.693}{1.04 \times 10^9} = 6.67 \times 10^{-10} \text{ sec.}^{-1}$$

$$N = \frac{1 \text{ g. Cs}^{137}}{137 \frac{\text{gram}}{\text{mole}}} \times 6.023 \times 10^{23} \frac{\text{atom}}{\text{mole}} = 4.38 \times 10^{21} \frac{\text{atom}}{\text{gram}}$$

$$\text{activity} = N\lambda = 4.38 \times 10^{21} \times 6.67 \times 10^{-10}$$

$$= 2.92 \times 10^{12} \text{ disintegrations/sec.}$$

$$= \frac{2.92 \times 10^{12} \text{ d/s}}{3.7 \times 10^{10} \frac{\text{d/s}}{\text{curie}}}$$

$$= 79 \text{ curie per gram Cs}^{137}$$

Then, the activity of a clay source containing 0.087 g. Cs^{137} per gram of clay is

$$\text{source activity} = 79 \frac{\text{curie}}{\text{gram Cs}} \times .057 \frac{\text{g. Cs}}{\text{g. source}}$$

$$= 4.5 \frac{\text{curies}}{\text{gram}}$$

The density of the clay source is estimated to be 2.2 g./cc. This is based on the assumption that the pulverized and compressed clay will be slightly less than the natural density of 2.348 g./cc (10).

For a 1000 curie source	}	Weight = $\frac{1000 \text{ curies}}{4.5 \text{ curies/gram}} = 222 \text{ grams}$
		and Volume = $\frac{222 \text{ grams}}{2.2 \text{ grams/cc.}} = 100 \text{ cc.}$

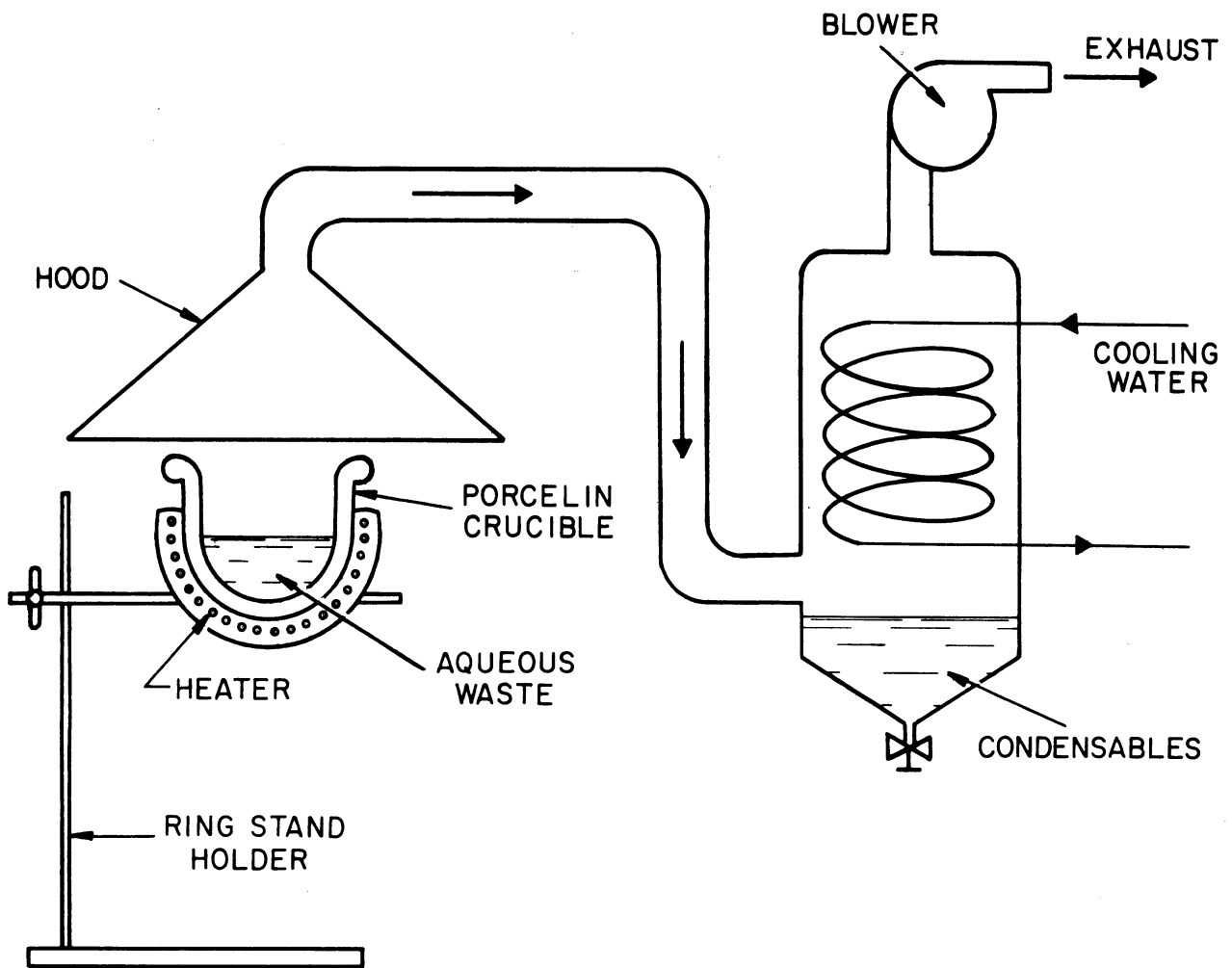


Figure 1. Equipment for Solidifying and Calcining Aqueous Waste

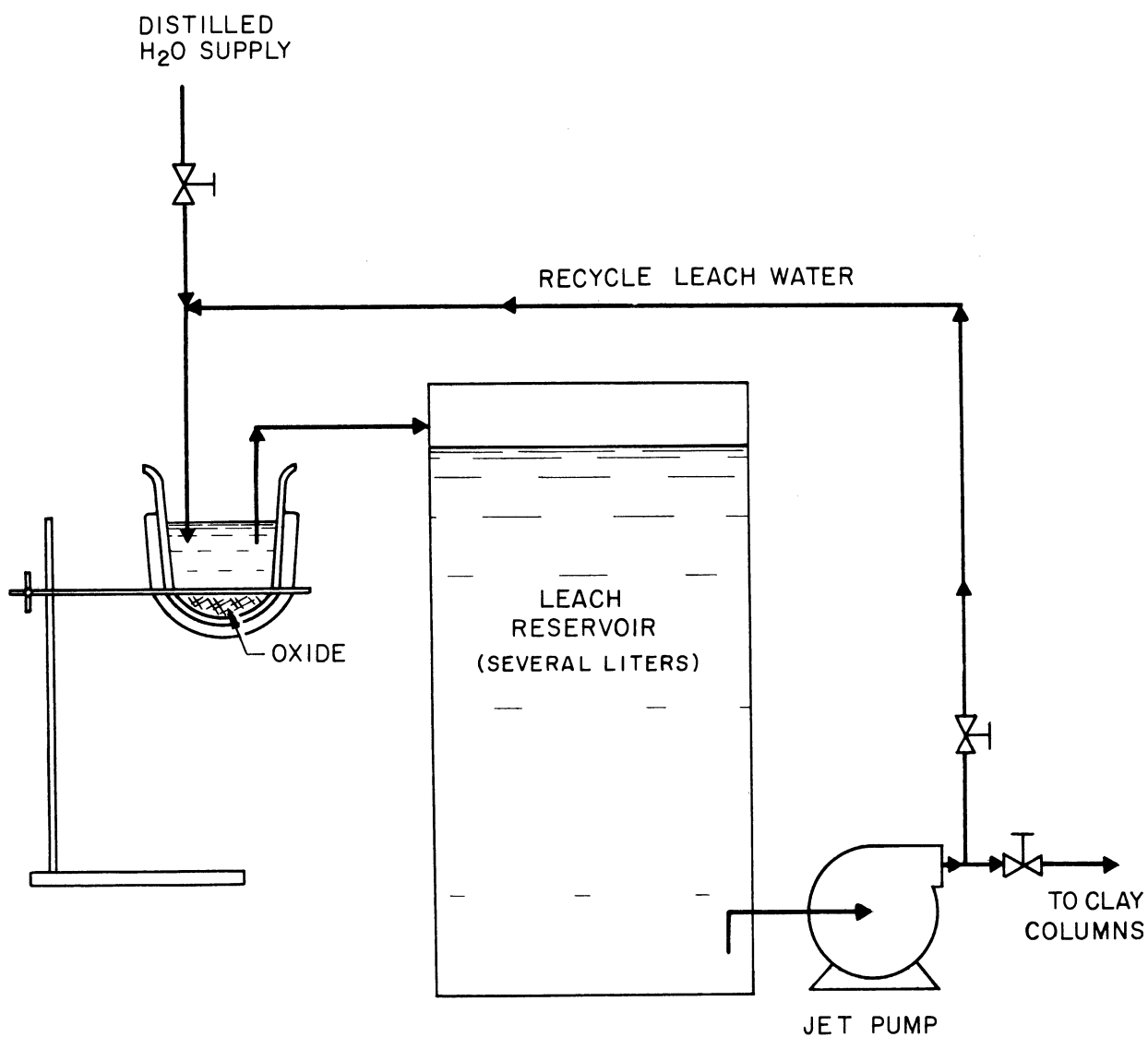


Figure 2. Leaching Apparatus

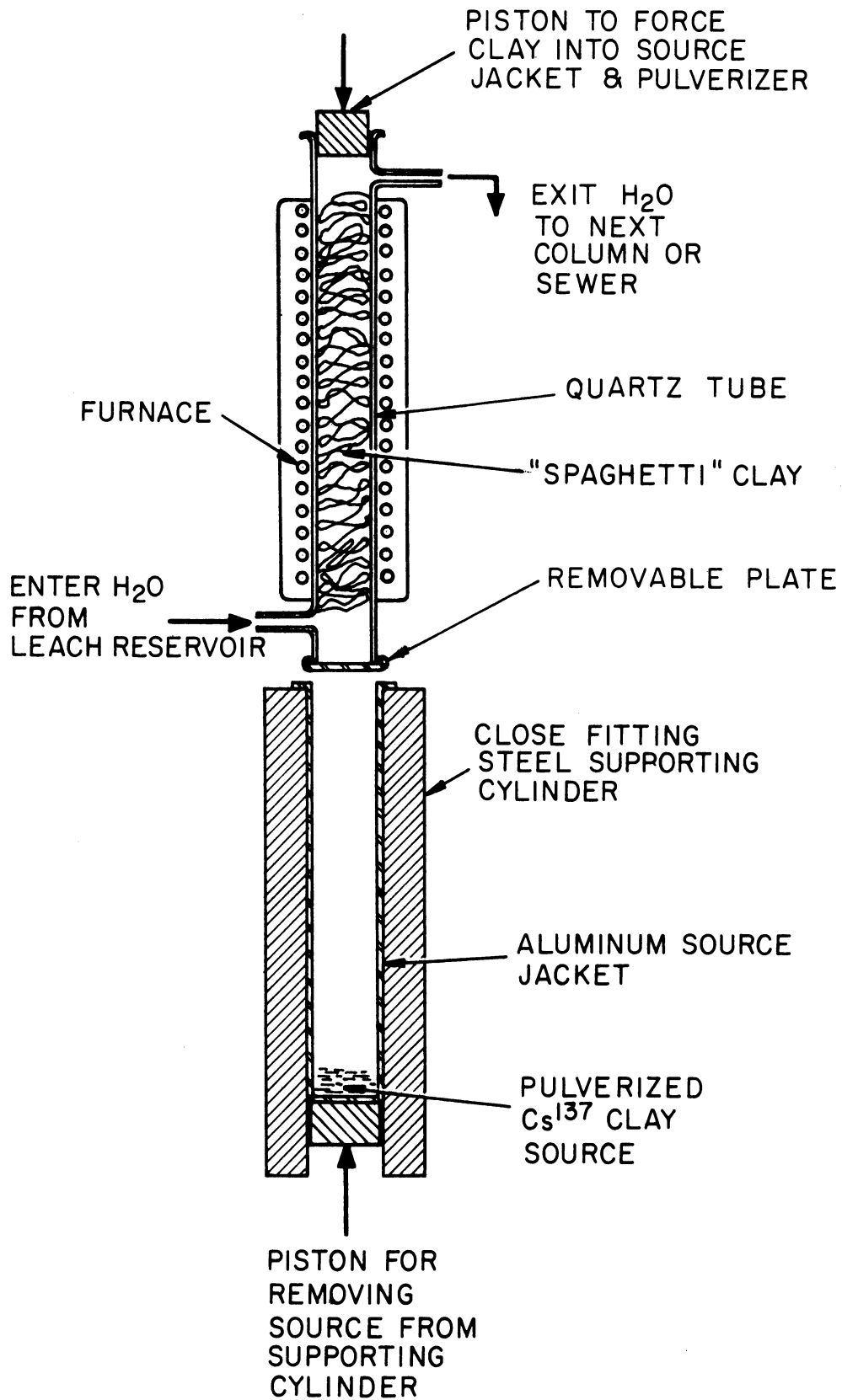


Figure 3. Adsorption and Source Loading Equipment

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