

**Removal of Cesium from Spent Nuclear Fuel Destined for the Electrefiner
Fuel Treatment Process**

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Executive Summary:

Cesium 137, a radioactive component comprising just 0.0027% of the total composition of used nuclear fuel, causes storage problems by generating nearly half of the total short-term heat emission of the waste by its nuclear decay. It is therefore desirable to remove cesium from the spent fuel prior to the fuel disposal in a long-term storage facility.

The objective of this design project was to modify the existing electrorefiner pyrochemical fuel treatment process to separate out the cesium.

Several different designs were researched and one ultimately chosen that had the following relevant operations (listed in consecutive order):

- The spent fuel is oxidized in a furnace at 500-700°C. This converts UO_2 to U_3O_8 and causes swelling, which ruptures the cladding and pulverizes the fuel.
- The oxygen atmosphere gets withdrawn by means of a pump with argon slowly passed through. The furnace temperature is then increased to 950°C, which will vaporize the cesium, separating it from the majority of the fuel. Filters are used to keep the uranium particles from leaving with the argon.
- The cesium is separated from the spent fuel using a series of three zeolite canisters. The zeolite used is 4A, and the stainless steel canisters can be welded shut for use in the long-term storage of the cesium contained within. Once the unit nearest the furnace reaches saturation, it is removed and prepared for storage while the remaining series gets shifted counterflow to the feed stream with a fresh unit replaced at the end.
- An activated charcoal filter is used to catch anything that breaks through the zeolite series.
- Finally, the remaining fuel left in the furnace is compressed using a die and press to increase the particle size to the 45 μm that is necessary for the oxide reduction step, and the resulting particles get sent into the oxide reduction step of the electrorefiner process.

The proposed design was built to handle 20 kg in a batch and it takes about 8 hours to process a batch. A bench scale design built to handle 500 g was also included in the design for testing several key processing concepts.

It is estimated that the full-scale process capable of preparing 90,000 tons of fuel for the electrorefiner process over the next 30 years would cost \$7.7 billion not taking into account the time value of money. The estimated total capital investment amounted to \$1.1 billion. The annual cost of our recommended operation amounted to \$6.6 million/year (neglecting the time value of money) with a cost of processing rods equal to \$2.30/kg of processed fuel. The above ground storage cost estimate equaled \$1.4 billion. The estimated cost of not doing anything or placing the waste directly into long-term

storage would cost about \$43 billion over the next 30 years. To verify the results of the study and prove the design's economical viability, it is recommended that a bench-scale experiment be performed.

1. Introduction

Nuclear spent fuel consists of uranium, transuranics, and fission products such as cesium, strontium, neodymium, cerium, lanthanum, barium and many others [1,2]. In commercial spent fuel, most of these materials exist in oxide form inside a metal cladding.

Nuclear reactors produce ^{137}Cs as one of their many waste products. Due to ^{137}Cs 's short half-life of 30 years, its radioactive decay generates significant heat over a relatively short period of time. Heat production is considered to be the major capacity limiting factor for the proposed Yucca Mountain long-term waste repository [2]. This means that it would be beneficial to remove ^{137}Cs from the spent fuel prior to disposal in the long-term facility. The ^{137}Cs could then be stored in a short-term facility while it radioactively decays into safe materials. From **CHARTS 1 and 2** it is apparent that while cesium makes up only a tiny fraction of the spent fuel, it and the meta state of barium it produces will generate about half of the total heat output of the spent fuel over the next 100 years. Since ^{137}Cs produces nearly half of heat that will be released from the waste over the next hundred years, removing it will effectively double the capacity of Yucca Mountain.

CHART 1: Typical concentration of PWR spent fuel 10 years after removal [1]

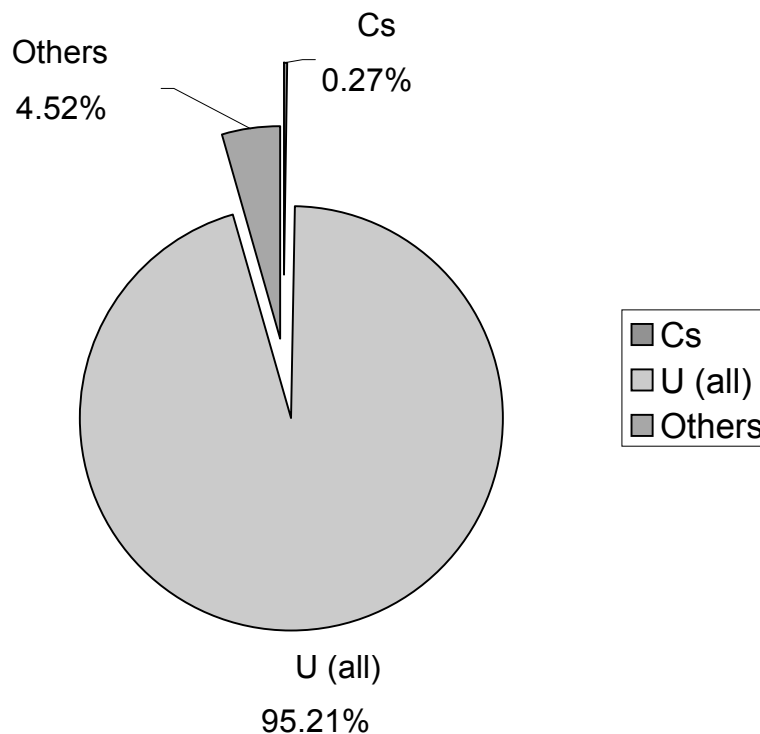
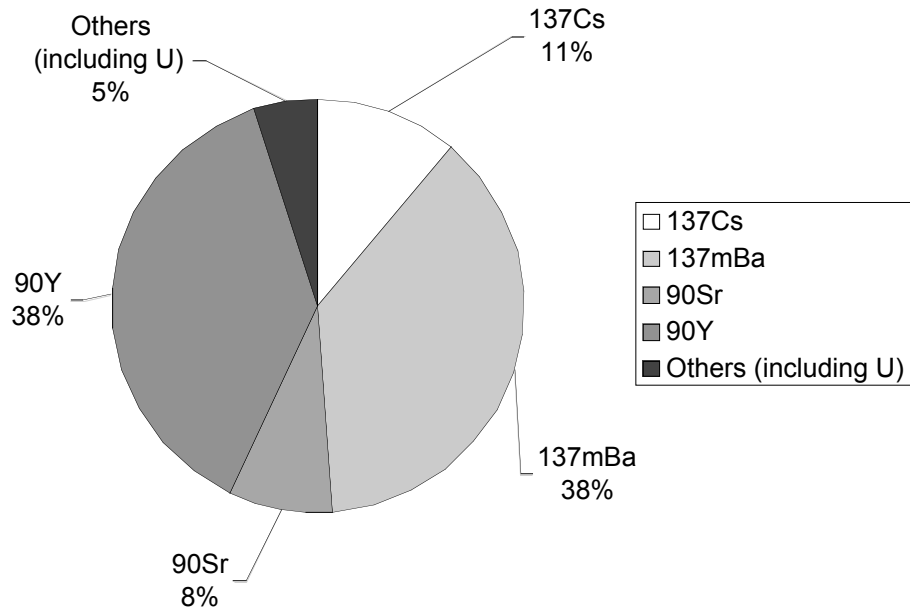


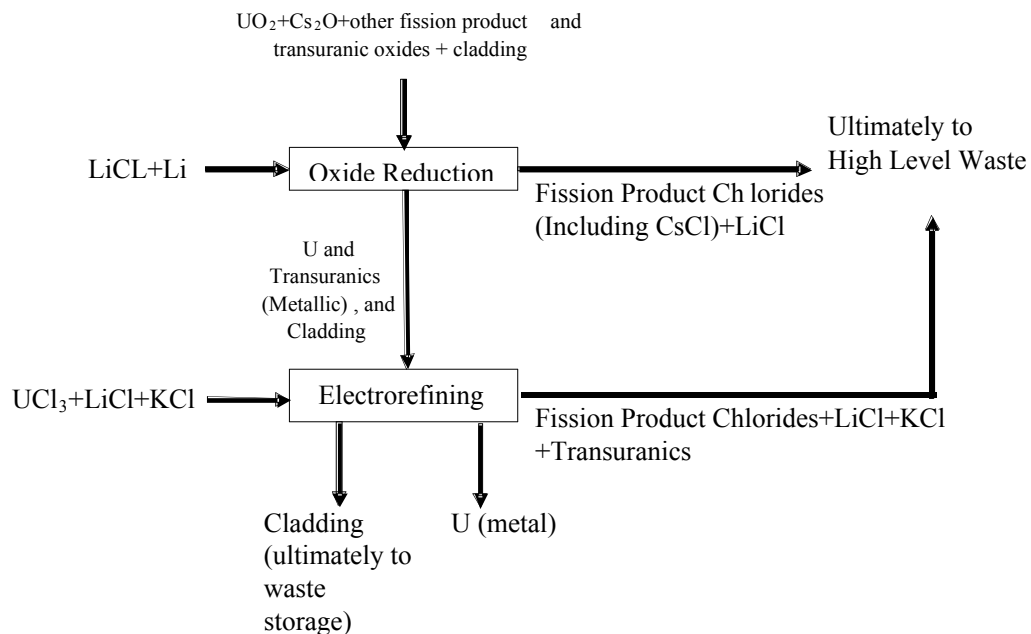
CHART 2: Fraction of total energy released over the next 100 years in PWR spent fuel [1]



The other products that contribute significantly to the short-term heat production are ^{90}Sr and its decay product ^{90}Y .

The electrorefiner process is an existing treatment process used to separate the transuranics from the fission products [3], allowing them to be recycled and reducing the amount of space required for storage. **FIGURE 1** gives an overview of the process.

FIGURE 1: Electrorefiner spent fuel treatment process



Currently, chopped fuel rods (still clad) are placed in a molten lithium chloride salt at 700°C along with pure lithium; the lithium reduces the oxides in the spent fuel to metal, and the resulting lithium oxide is then dissolved in the salt. Several fission products are also dissolved in the salt as chlorides, notably cesium. This process is called oxide-reduction [4]. The remaining components, which are now reduced to a metallic form and consist primarily of uranium, are passed through an electrorefiner, which consists of an anode (which holds the metallic fuel and cladding) and a cathode (where the uranium collects) in a salt solution consisting of lithium, potassium, and uranium chlorides. The electrorefiner separates the waste into three products: uranium, cladding (which remains in the anode), and chloride salts of fission products and transuranics (TRUs) that are located in the molten salt phase. The cladding is then processed and sent as a metallic waste form to long-term storage. The fission products and the transuranics are separated from the other salts and sent to long-term storage and the salts recycled; salts from the oxide reduction step may also be processed and recycled; the uranium may be stored or reused. Any separation process for removing the ^{137}Cs would have to be compatible with this existing treatment process.

Currently it's projected that 90,000 metric tons of spent fuel needs to be processed in the next 30 years [5]. The amount the electrorefiner can process is limited by the criticality of the products. Currently it is estimated that one batch in the electrorefiner must be limited to less than 300 kg of uranium in order to avoid a potentially critical mass collecting at the cathode. However the engineering scale process that is currently being tested is limited by the oxide-reduction throughput of 20kg in 8 hours [6].

The goal of this project is to develop a process for removing ^{137}Cs from spent nuclear fuel. The benefits of using such a process to increase the capacity of long-term storage facilities will then be determined. Any preprocessing required of the clad fuel rods (i.e., chopping, punching, cutting, etc.) will not be considered nor will the separation of non-cesium fission products that may be removed in any process. However, it must be ensured that neither TRUs nor uranium are separated with the cesium.

2. Overview of Possible Methods of Separation

The possible methods to separate cesium were broken into two groups, separations before the oxide reduction step and separations after it when the cesium is located in the molten salt. The post-oxide reduction options were then further broken up into two groups, separations after converting the molten salt into an aqueous phase and separations directly in the molten salt phase.

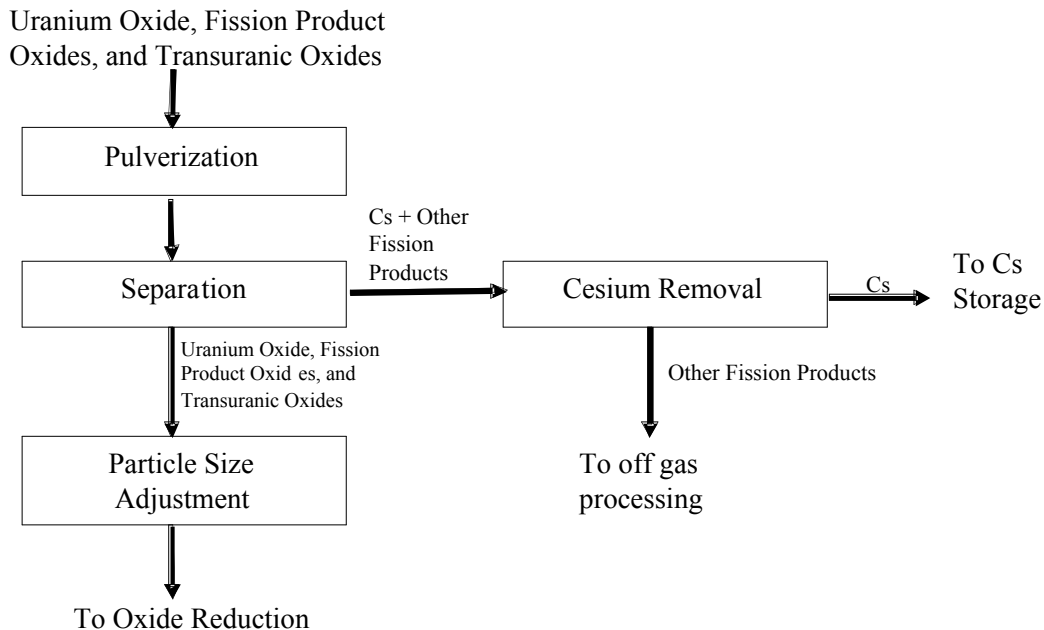
2.1 Pre Oxide Reduction Separation

Since working with molten salts is more difficult than working with solid fuel, it may be desirable to remove the cesium from the spent fuel before the Oxide Reduction step. There are two ways to do this, physically or chemically. Any chemical separation would introduce undesirable components such as water into the electrorefiner process

unless expensive removal steps are used. Therefore, only a physical separation process is considered.

A flow diagram of a physical separation process is presented in **FIGURE 2**. The first step is to convert the fuel into a usable form, as the cesium is currently trapped within the uranium oxide. Either pulverizing or melting the uranium oxide can do this, but since melting the uranium oxide requires very high temperatures ($> 2800^{\circ}\text{C}$), pulverization is the better option. Once this is done, the cesium oxide must be separated from the other oxides. The most straightforward separation is heating under a vacuum to vaporize the cesium oxide. The vaporization process works on the large difference in the vapor pressure many of the TRU oxides and the cesium oxides [7,8, APPENDIX G]; however, some TRUs such as americium oxide have vapor pressures similar to cesium. These may also be vaporized, and a method may be required to separate them from the cesium vapor. This was found not to be the case, to prevent removal of Americium Oxide from the spent fuel, the furnace will be operated below 1000°C . Since the remaining oxides must be used in the electrorefiner process, the fuel must be converted into particles at least $45\text{ }\mu\text{m}$ in size for use in the electrorefiner process [9].

FIGURE 2: Physical Separation before Oxide Reduction Step



The main benefit of removing Cs from the spent fuel before the Oxide-Reduction step is easier handling than the molten salt, however working with the solid fuel has the drawback of requiring more processing of fuel components such as UO_2 , TRU oxides, and the cladding.

2.2 Aqueous Phase Separation

Extensive research has been conducted on removing dissolved cesium ions from an aqueous phase. Excellent separation may be achieved through the use of crown ethers [10], mesopores, solvent extraction and ion exchange, and organic solvents [11,12].

However, the high cost of drying the resulting precipitates and solutions would likely be cost-prohibitive. Moreover, the cesium chloride molten salt must be converted into an aqueous phase before the separation can occur.

The primary benefits of an aqueous phase process are that good separation methods are easy to find, and a large amount of data is available. Several methods may be able to remove the strontium along with the cesium; if it were economically feasible to perform an aqueous phase separation that removed both strontium and cesium, the overall heat output over the next 100 years would be reduced by 95%, instead of just 49%. Another benefit is that only the waste that is soluble in the molten salt must be treated.

The main disadvantage of an aqueous phase separation is the excessive cost of putting the molten salt into an aqueous phase and the drying of the separation products. Large amounts of water would also be required to dissolve all of the lithium salt, and this would translate into a large volume, which is bad for a process that must be carried out in a hot-cell.

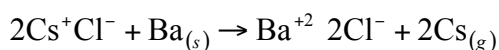
2.3 Separation in the Molten Salt Phase

The chemical separation of ^{137}Cs directly from the molten salt phase presents many challenges since the work involved in this separation approach has for the most part not been investigated.

As shown in **FIGURE 1**, there are two streams of molten salts: one exits from the oxide reduction step while the other comes from the electrorefining process. Since the majority of the cesium is expected to dissolve in the stream exiting the oxide reduction step [2], it is this stream that is of primary concern for the separation of ^{137}Cs . This molten salt phase is expected to contain three main categories of species; the rare earth species or actinides, noble metals, and fission product (FP) series [4]. The cesium chloride is classified as a FP.

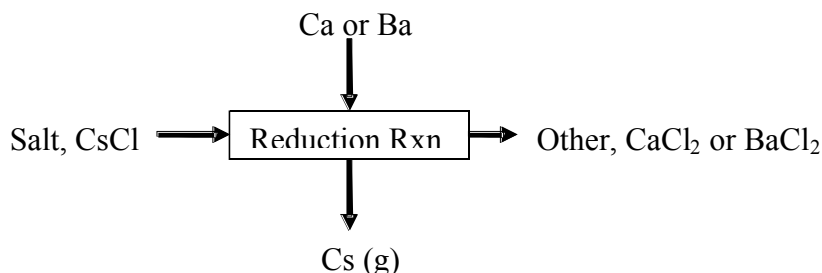
2.3.1 Separation using Reduction Reaction in the Molten Salt Phase

Although most work on separating cesium chloride salts in radioactive molten phases has not been documented, it is known that ordinary cesium chloride salt may be reduced by pure barium in the following reaction [13]:



It is also possible for calcium to act as a suitable substitute in place of barium in the reduction. Although this reaction may work for pure metal and cesium chloride salt, this may not always hold true for radioactive metal and salt mixtures that present additional challenges for the separation (i.e., several other metal and salt species in abundance and Cs isotopes). The separation procedure utilizing this reaction is depicted below in **FIGURE 3**.

FIGURE 3: Flow Chart of the reduction reaction separation of cesium from the molten salt phase.



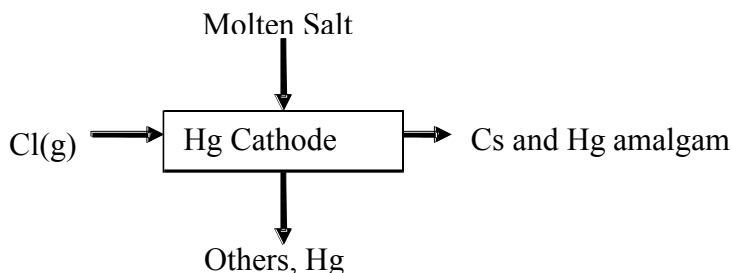
The exchange reaction proceeds at 700°C and generates Cs vapor at 500°C. The vapor could then become condensed and stored in an oil reservoir as metallic cesium. This separation method is particularly attractive since the products from the reaction are the same chloride salts as was in the initial FP stream prior to the reaction: It is a simple exchange in the metal species ionically-bonded with the chloride species in the salt form; cesium is traded for the barium or calcium by virtue of differences in electronegativities between these reacting metallic species.

However, the chemical separation method of using the calcium/barium reduction reaction does present some drawbacks, including possible undesired or uncontrollable side reactions, the desired reaction of CsCl reduction not reaching completion (i.e., Ba or Ca reacting with other species or Cs isotopes in the FP mixture), and the general present lack of data and documented reliability of chemical reaction separation processes of spent LWR fuel.

2.3.2 Electrochemical Method of Separation

Another chemical separation method of Cs employs the use of mercury cathodes. In this approach, concentrated cesium salt gets electrolyzed on the cathode such that it becomes an amalgam [11]. This process is analogous to an electrorefining procedure in that a species is transferred from the molten salt onto a cathode. However, instead of depositing on the surface of the cathode, it forms an amalgam with the cathode. The basic flow of this process is depicted in **FIGURE 4**.

FIGURE 4: Mercury cathode flow chart



An obvious disadvantage to the mercury cathode approach is that mercury will leak out into the product streams, which presents a new purification initiative that will ultimately require cesium separated from mercury as well as the rest of the impurities within the exiting cesium stream. Furthermore, mercury is a liquid waste, so it must also

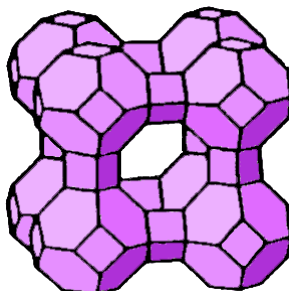
eventually get separated from even the radioactive waste streams that do not contain cesium. Hence, the mercury cathode separation method is an undesirably expensive and time-consuming process.

The chemical separation approach overall does present some attractive advantages. The chemical reaction method is an energy efficient separation; at the core of this method, it exploits chemical affinities or differences and reaction equilibrium so as to make the process go on its own instead of applying brute force energy. A major disadvantage of this overall approach comes from the fact that although either the reduction or mercury cathode reactions are possible for separating cesium from ordinary molten salt phases, no data yet exist on how either work in this context of separating radioactive ^{137}Cs from FP series or LWR spent fuel.

2.3.3 Molten Salt Separations using Zeolites

Zeolites are synthesized or naturally found nanoscale porous crystalline structures of hydrated aluminosilicates of the alkaline and alkaline earth metals characterized by their pore size and geometrical arrangement. Zeolite 4A (also known as *sodalite*) is a type of zeolite that readily adsorbs cesium chloride from molten salt phases, and a sodalite unit cell as depicted in **FIGURE 5** can on average contain three CsCl molecules [14].

FIGURE 5: Unit Cell of Zeolite 4A or *sodalite*



Using this estimate of the amount of CsCl removed per unit cell of zeolite 4A, a weight percent computation is made to find the ratio of the mass of cesium chloride adsorbed to the mass of adsorbent zeolite used for the separation:

$$\text{Adsorption wt\% (mass CsCl/mass zeolite 4A)} = \frac{3 \text{ CsCl}}{\text{Na}_6\text{Si}_6\text{Al}_6\text{O}_{24}} = 0.509 \frac{\text{g CsCl}}{\text{g Z}}$$

Since zeolite 4A is more economically viable compared to other processes such as barium reduction and electrochemical separation using mercury cathodes, the zeolite separation method is an effective option for handling molten salt streams from pyroprocesses.

Using zeolite 4A directly after the electrorefiner such that the cesium chloride is adsorbed in situ will allow the electrorefiner salt to be recycled. But the challenge behind this approach is how to remove trace amounts of uranium from the zeolite; a pure molten

salt phase without uranium would need to be “flushed through” the zeolite to sweep away the remaining or residual uranium from the zeolite network. An added economical and energy cost will be needed to implement this step, and it is possible that some uranium may get trapped in the zeolite network, which can call into question the efficacy of this approach before it is even used.

2.4 Conclusion

The best two options for separating ^{137}Cs from the spent fuel are the zeolite separation in the molten salt phase and the physical separation before the oxide-reduction step. Both approaches were previously tried and tested, exhibiting their own advantages and future challenges. However, due to scope of this design project, only one of the two approaches could be chosen. The physical separation approach was selected due to its relative simplicity ease of integration with the existing process.

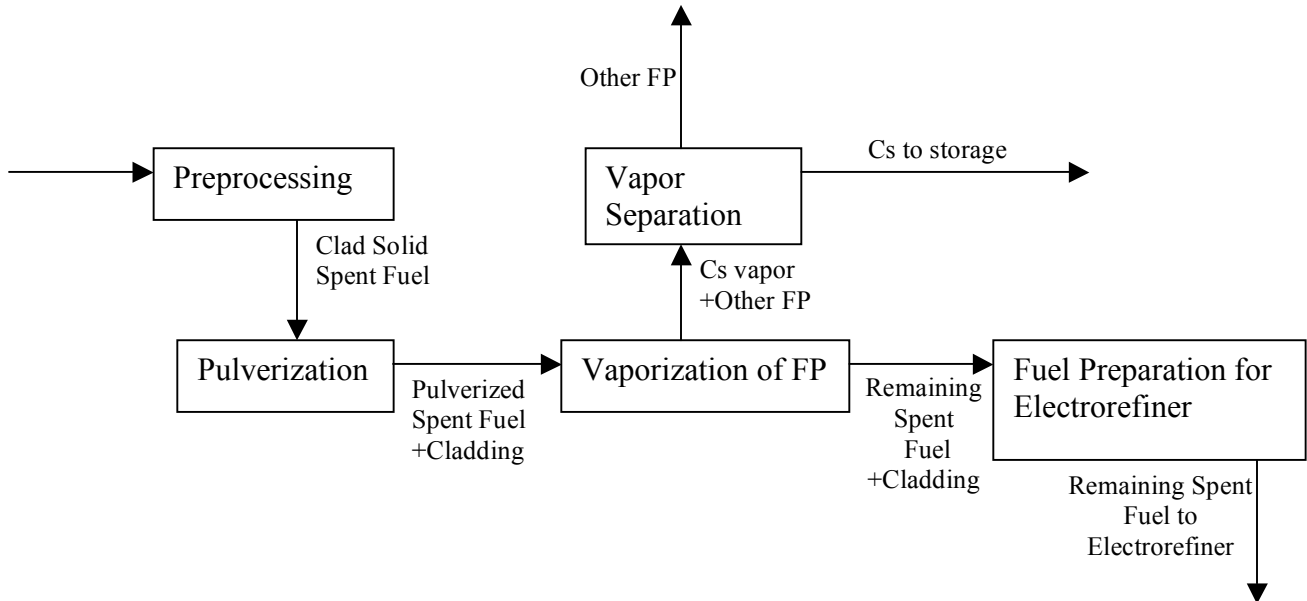
3. Design Considerations for Pulverization and Vaporization

The necessary components for the physical vapor separation process that occurs before entry into the oxide-reduction step are **[FIGURE 6]**:

- a system to cut, puncture or otherwise preprocess the clad fuel rods.
- a system to pulverize the fuel,
- a system to vaporize the cesium,
- a system to perform a separation of the resulting cesium oxide vapors
- and a system to prepare the fuel for entry into the electrorefiner process.

The preprocessing of the fuel (a) will not be considered in this report since it is the same as required for the electrorefiner process.

FIGURE 6: Flow diagram of the process.



The overall material balance for a reference system capable of processing 20 kg of spent fuel is given in **TABLE 1**.

TABLE 1: Estimated Overall Mass Balance on System
(for 20 kg of processed fuel w/o cladding)

	Input (g) [1]	Output (g)				Balance
	Spent Fuel	Spent Fuel	Zeolite	Activated Charcoal	Filters	
Cladding	2000	2000				0.0
Molybdenum	70		70			0.0
Palladium	28	14	14			0.0
Silver	2		2			0.0
Cesium	46		46			0.0
Tellurium	10	5	5			0.0
Rubidium	8		8			0.0
Iodine	4		0.0	4		0.0
Uranium	19218	19218			?	0.0
Others	614	614			?	0.0
Total	2200	21851	145	4	0	0.0

3.1 Pulverization:

Since the cesium is mixed into the fuel, the fuel must be pulverized to enable the release of the cesium. Two methods to do this are mechanical grinding and oxidation of the uranium oxide. Mechanical grinding has significant drawbacks such as contamination of the grinding surface, production of airborne particles, and moving parts that will wear out. This leaves the oxidation method.

The oxidation of UO_2 to U_3O_8 increases the volume and also causes the creation of small particles [15]. The decrease in density can be used to remove the cladding, and there exist several processes to do so. These processes include AIROX, voloxidation, and DEOX. AIROX and DEOX both use the oxidation to pulverize the fuel and remove the cladding, AIROX then uses a series of additional reductions and oxidations to create very fine particles suitable for sintering. Voloxidation is similar to DEOX except that a different temperature regime is used. However, even the DEOX process tends to produce particle sizes that are too small for use in the oxide-reduction step, which is currently limited to $45\text{ }\mu\text{m}$ and larger particles [6,16]. There are two solutions to this: either improve the capabilities of the oxide-reduction step to handle very small particles, or increase the particle size. Improving the capabilities of the oxide-reduction process to handle smaller particles is beyond the scope of this report; however, the other option will be addressed.

The particle sizes may be increased in two ways, either alter the oxidation process to produce larger particle sizes or add a separate process to increase the particle size after oxidation is done. The DEOX process was an attempt to do the former; however, current results have not been promising [16]. If alterations can be made to the oxidation process that would result in sufficient particle size, DEOX is preferred over other methods, but since the experimental results for the DEOX process are not good, the final recommended design will include a process to increase the particle size after oxidation.

Since the particle size is no longer a big constraint (it will be increased before entry into the oxide reduction process), it is possible to use a series of oxidations and reductions similar to the AIROX process to remove the fission products more effectively [15]; however, since the AIROX greatly reduces particle size and there is some hope that the DEOX process can be made to produce the correct particle sizes or the oxide reduction step modified to handle smaller particles (and thus skip an expensive step to increase the particle size) the final recommended design will closely match the DEOX process.

3.2 Cesium Vaporization:

Once the fuel has been pulverized, the next step is to extract the Cs from it. Since the oxidation process occurs at high temperatures (about 500-700°C [16]), FPs will be vaporized during the oxidation; however, the exact amounts of FPs released depend on a number of factors such as the pressure used, the temperature, the degree of pulverization, and the extent of oxidation [17]. Since all of the fission products may not be released during oxidation, it is necessary to have a step in which the cesium is removed through vaporization. This must be done at high temperatures (>700°C) and moderate to low pressures. Since high temperatures are used, an oxygen atmosphere cannot be used since oxidation (and pulverization) of the cladding could occur above 700°C [16]. Therefore, an inert atmosphere (probably argon) will have to be employed. Once again it is impossible to tell the rate at which the fission products will be released since among other things it is a function of the particle size resulting from the pulverization step, but based off of data from the AIROX process it will take several hours to remove the majority of the cesium [15,16,18]. To create sizing estimates for the separator system, it was estimated that the entire amount of cesium (~12g/rod, see **APPENDIX E**) would be released over five hours with a peak rate of twice the average rate. This is a very inaccurate guess, and the equipment may need to be resized based on the results of kinetic experiments.

It is desirable to perform this vaporization at as high of temperature as possible to improve removal rate. Since the decomposition of cesium oxide occurs at around 1000°C [8] and may create problems during subsequent separation steps; it is necessary to carry out the vaporization slightly below 1000°C. Additionally, several TRUs such as americium may be vaporized above 1000°C, and experiments must be carried out to make sure that they are not also vaporized at the final temperature selected. The final temperature selected will be between 700°C and 1000°C.

3.3 Sizing of the Furnace:

The next step is to size the furnace required. An estimate of the exterior dimensions is obtained from the size necessary for the DEOX process testing of approximately: 30 cm³ / gram of fuel processed [17,19]. It is then assumed that the processing rate will be linear with furnace volume. The criticality limit in the furnace is very high, however the amount of uranium in the furnace should be limited to less than 300 kg so a single batch can be used in the electrolyzer.

3.4 Particle Size Increase:

There are several methods to increase the size of UO₂ particles. These methods include compression, melting, and sintering [20]. There are also several other exotic

methods that may be suitable for use in this process, the most prominent being the use of a binder or chemical reagent that creates an appropriate particle size and is removed by the lithium chloride salt solution during the oxide reduction leaving large metal particles. Another method is to reduce the mixture to metals and then melt, or compress it in order to create a substance suitable for use in the electrolyzer (the oxide reduction in lithium chloride salt solution is not necessary).

Direct melting is probably the least useful technique since it requires temperatures above 2800°C [7] and then cooling to temperatures where it can be handled which will take considerable time. Its benefits are that it can be carried out in the same furnace as the other steps (provided the furnace can get up to the required temperatures), it will change the U_3O_8 created by the oxidation to UO_2 which has been tested in the oxide reduction step (it also produces UO_3), and it will definitely produce particles greater than the required 45 μm . However the particles may be too large, increasing the time to reduce the oxide to a metal. The system must be sealed during this process to prevent release of vapor containing vaporous TRUs and FPs from the furnace.

Compression at a moderately high temperature may be a better option but the compressibility of UO_2 is not readily available, so the usefulness of this technique is unknown. Sintering after compression is almost assured to create the correct fuel sizes since this is the technique used to create most fuel rods. Those particles were probably better for the sintering process but sintering should still ensure adequate particle sizes. This may or may not require binders, more research and some experimentation is needed to find out if binders are required and if the resulting material will be suitable for use in the oxide reduction step. Additionally the use of compression at moderate temperatures requires a die compaction machine in order to apply pressure to the powder.

The use of a binder or chemical reagent that is removed during the oxide reduction step is probably the best technique since it requires neither high temperatures nor expensive equipment, however no suitable reagent has been found. Additionally purification of the molten salt will be required to remove the reagent from the system.

Reduction to metal using a series of chemical reactions to facilitate larger particle size offers many advantages such as not requiring LiCl salt at all, but requires extensive research and experimental testing before it can be recommended for use. It also has the disadvantage that several chemical reagents are likely required for use.

Based on the possible methods, the method currently recommended for bench scale testing is the compression at moderate temperatures, this is because it is likely to work and it is well understood. It is however recommended that all the techniques be investigated more fully along with modifying the oxidation process to produce larger particles and modifying the oxide reduction process to accept smaller particle sizes.

3.5 Additional Considerations:

Since the small particles of uranium oxide may become airborne it is necessary to have a filter to prevent them from escaping the process. This filter must be able to remove particles less than 45 μm in size (the smallest particle to be removed must be determined experimentally since the experiments that determined the particle size stopped at 45 μm) and also be able to withstand oxygen at up to 700°C, and argon up to 1000°C. A 625 (20 μm) or 1250 (10 μm) mesh screen made of a corrosion resistant

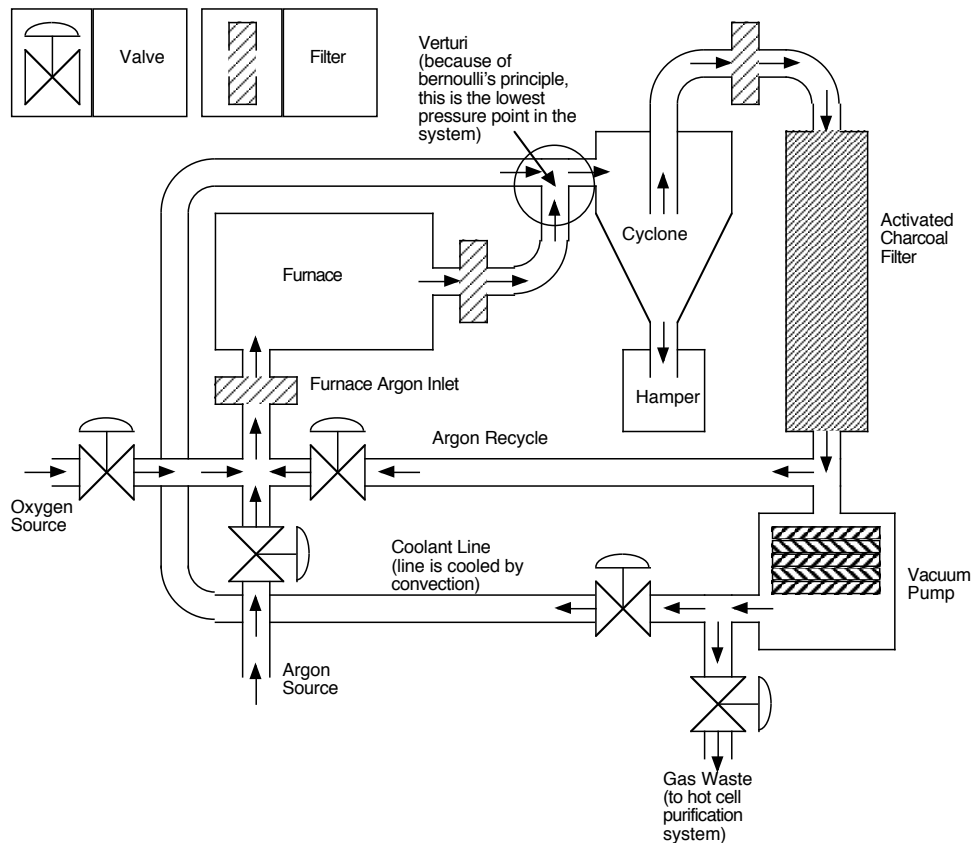
material should be adequate when provided with slow flow rates of the gasses moving through the furnace.

3.6 Vapor Separation

In order to separate the cesium oxide from the gas stream, it must be cooled, and the resulting solid must be separated from the gas stream, or it must be entrapped in a zeolite bed. There are two workable methods to cooling the gas stream: direct contact with coolant and indirect contact with coolant. Regardless of the contact method, conventional filters would need to be provided after the furnace to prevent contamination of the off gas stream with uranium oxide particles and after the cesium oxide separator to prevent cesium oxide particles from entering the secondary separation (which is used to remove the iodine).

In direct cooling, the hot off gasses from the furnace would be mixed with a cool argon stream in a venturi vacuum. This would cause the cesium oxide, as well as some of the other less volatile components to form a solid precipitate. Precipitate size would be determined by coolant and off gas temperature and flow rate, as well as the flow characteristics of the venturi. The resulting precipitate could be filtered using a series of conventional filters, or by a cyclone. The cyclone is the best option if workable, since it produces the most compact form of waste. **FIGURE 7** depicts this process.

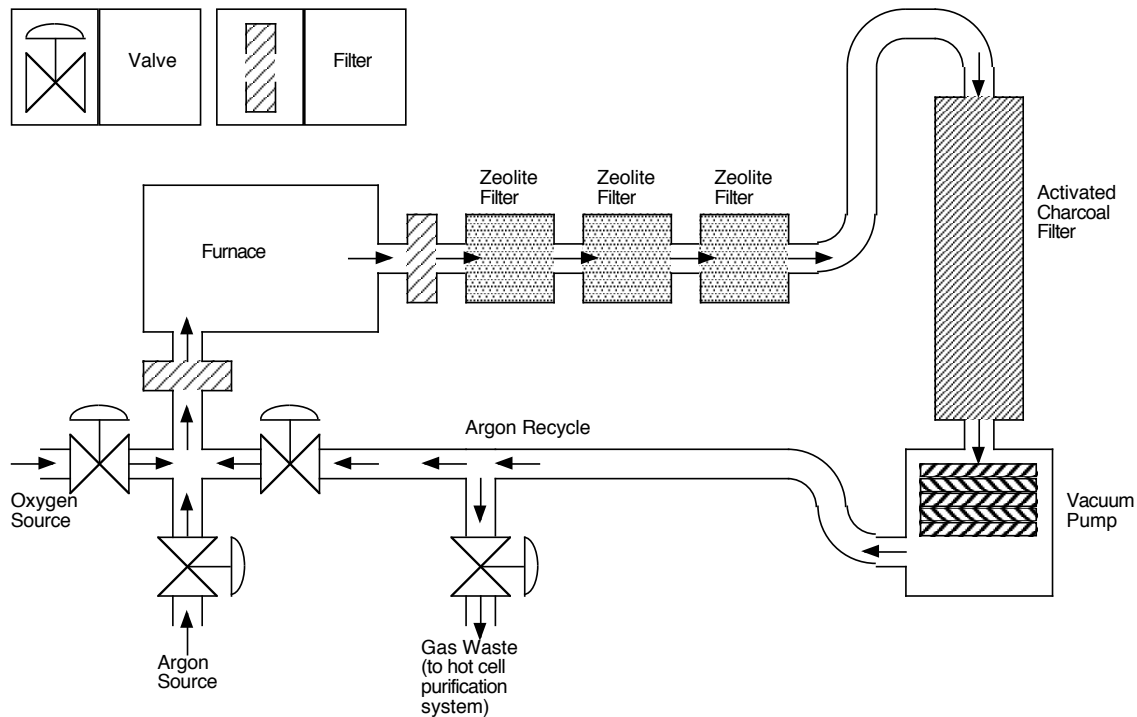
FIGURE 7: Cyclone Separation Schematic



Indirect cooling would involve passing the hot gas stream over a cool heat exchange surface. The cesium oxide would then precipitate directly onto the cooling surface. A system would need to be devised to remove the oxide from the surface, or the surface would need to be routinely replaced as buildup occurs. This is not likely a good option since a large surface area would be required, and routine maintenance would be necessary.

Zeolite filtration would likely use zeolite 4A. The gas stream would get passed through and then heat the zeolite so that a number of successively cooler beds would be used in series to remove all of the cesium oxide. The cesium oxide would adsorb onto the surface of the zeolite. Once breakthrough is achieved, the hottest bed would be removed and sent to storage, the beds would be moved forward, and a new bed would be added at the end of the system. Other oxides would precipitate as the temperature decreases, as well as adsorbing to the zeolite. Zeolite separation is a good option because it requires no moving parts, and only an entering filter assembly. On the other hand, it does not produce compact waste. **FIGURE 8** depicts this process.

FIGURE 8: Zeolite Separation Schematic



3.6.1 Direct Contact

Assuming that the direct cooling method is the best, and the cyclone separation method is the most economical, the cyclone size depends on many factors. The size of cyclone required depends on particle size, desired separation, vacuum applied, and inlet flow rate and composition [21]. The inlet velocity and the cyclone diameter will determine the centrifugal force that leads to separation. Unfortunately, particle size is unknown. Cyclones are typically used to separate particles between 40 and 400 microns

in size, and may be used to remove particles as fine as 5 microns in size. The applied vacuum can be altered to allow for better or worse separation depending on optimal operating conditions. The optimal separation depends on the relative cost of storing saturated filters over pure cesium oxide waste, and vacuum pump operating cost. It is easy to see that some experimentation is necessary to determine the proper size of cyclone. Standard cyclones range in size up to three feet in diameter and up to ten feet in length. It is likely given our flow rate that the required size is relatively small. The cyclone will almost certainly be less than 3 cubic feet in volume.

Cesium removal would be simple, the bottoms from the cyclone would be collected in a filter bag, and the filters on either end of the cyclone would need to be replaced periodically to promote flow. The resulting cesium oxide would be very concentrated. It would produce approximately 121,000 ci/kg cesium oxide (for reference the upper limit for Class C radioactive waste is 3 ci/m³, cesium oxide has a density of 4650 kg/m³). Further it would produce about 840 W/kg heat, assuming that any appreciable amount is stored in a storage container, this will lead to storage problems. It is safe to say that nothing is gained by storing cesium oxide in such a compact form. It would need to be stored in very small containers to prevent corrosion and melting of the container, or would require active cooling in the short-term storage facility, adding dramatically to the cost of short-term storage. The cesium will need to be stored over a large area of ground, regardless of how compact it is.

3.6.2 Zeolite Separation Procedure:

Zeolites can also be used to separate cesium oxides from the off gas stream. Zeolite 4A is a type of zeolite that can not only readily adsorb cesium chloride from molten salt phases, but it can do similar for separating cesium oxide species from fission product streams [22].

Still, an exact quantifiable number of the cesium oxide weight percent adsorption capability of zeolite 4A remains under investigation. However, previous work has shown that zeolite 4A is even able to contain large (Cs₄)⁺³ clusters in the amount of one cluster per unit cell [23]. Assuming that a (Cs₄)⁺³ cluster, which is a very large molecule compared to the largest cesium oxide species possible in the product stream, acts as the analog of the largest of the cesium oxide species, a conservative approximation can be made in estimating the adsorption weight percent of the mass of CsO_x per mass of zeolite. Assuming the largest oxide species is Cs₂O, this species now becomes the (Cs₄)⁺³ cluster analog, allowing the approximation to be computed as:

$$\text{Adsorption wt}\% \approx \frac{1 \text{ (Cs}_4\text{)}^{+3}}{\text{Na}_6\text{Si}_6\text{Al}_6\text{O}_{24}} : \frac{1 \text{ Cs}_2\text{O}}{\text{Na}_6\text{Si}_6\text{Al}_6\text{O}_{24}} = 0.330 \frac{\text{g Cs}_2\text{O}}{\text{g Z}} \leq N \frac{\text{g CsO}_x}{\text{g Z}}.$$

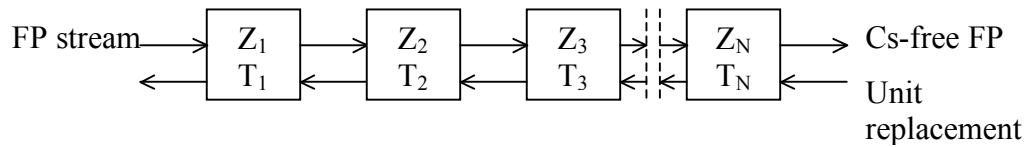
About 12 g of cesium oxide (**APPENDIX E**) is located within a fuel rod. On a per fuel rod processing basis, the amount of zeolite needed to separate this amount, using the above-mentioned conservative estimate, equals about 45.5 g or 0.10 lb_m. Using an average bulk density for the zeolite of 43.1 lb_m/ft³ [24], the volume of each zeolite unit

should equal 0.002 ft³/rod or 3.84 in³/rod, or for a per kilogram basis, this translates into about 15.7 cm³/kg

Other volatile oxide FP species will adsorb on the zeolite surface, which inevitably increases the required amount of zeolite needed to separate out the FP. Hence, in the final economical analysis, the adsorption ratio calculated above was reduced by one-third.

The general design approach to treating the off gas volatile oxide product stream with zeolites for separating out the cesium oxides is a counterflow zeolite staging or unit operation system, depicted in **FIGURE 9**:

FIGURE 9: General Scheme of Zeolite Unit Separation.



As shown in **FIGURE 9**, each zeolite is run at a temperature of T_N, ranked as T₁ > T₂ > T₃ > T_N. The lower temperatures of the successive units enhance the separation as the streams become more dilute in cesium oxide. Each stage is also monitored with a radioactivity meter to determine when each unit reaches its saturation limit of containing cesium oxide. Zeolite unit 1 receives the initial or fresh offgas stream while the successive units capture the breakthrough of the stream exiting from the previous unit.

In the zeolite system, the primary variables of most concern are the flow rate of the gas stream entering the system and the pressure drop across each zeolite unit (modeled by a solid packed bed gas adsorber). Since the stages are sequenced in order of decreasing temperature, cooling requirements will also impact the recommended design. Also of consideration is the number of stages to provide the sufficient separation requirements. Special piping and instrumentation will be needed that is highly leakproof and resistant to being continually subject to the high temperatures at which the process operates under.

When each zeolite unit becomes saturated in cesium oxide as monitored by the radioactivity monitors provided by the hot cell space, the provided robot arm replaces it and the stage of operations gets shifted towards the concentrated end with a new zeolite cartridge loaded into the most dilute end. All saturated zeolites essentially become the waste products.

Furthermore, because the final waste will have a high radiation and heat output, the storage container for the zeolites containing the FPs will need to be highly corrosive-

resistant, possess good thermal conductivity, exhibit high leak resistance, and be able to be sealed or welded such that nothing can escape for an indefinite amount of time.

The final design will need to consider the exact number of stages, the temperatures of each of the stages that range from the temperature of the furnace (1300 K) to about 300 K (at the end of the separation process), and exactly how these temperatures will be maintained.

The temperature can be maintained within the desired range through the use of active cooling. The active cooling system will consist of a series of fans that will blow argon (assumed provided from the hot cell space) over the zeolite canisters at a velocity of approximately 0.5 m/s (see **APPENDIX F**).

3.6.3 Selection of Separation System

Based on the considerations in the design for the two different separation methods it is now possible to determine which system should be used. The zeolite separation system has a number of advantages over the cyclone system. First, it is a simpler design with fewer parts. As such it is easier to design, build, and operate. Second, it produces less compact waste, which simplifies heat concerns. Finally it has a slightly lower capital cost, and a significantly lower operating cost, as shown in **TABLE 2**. The cost of robotic manipulation was taken to be the same in either case, and is included in the staffing cost. It was assumed that the cyclone would require roughly 3 times the argon flow rate to achieve a similar rate of separation, and this flow rate would need to be supplied a pressure equal to the pressure supplied in the zeolite separation process.

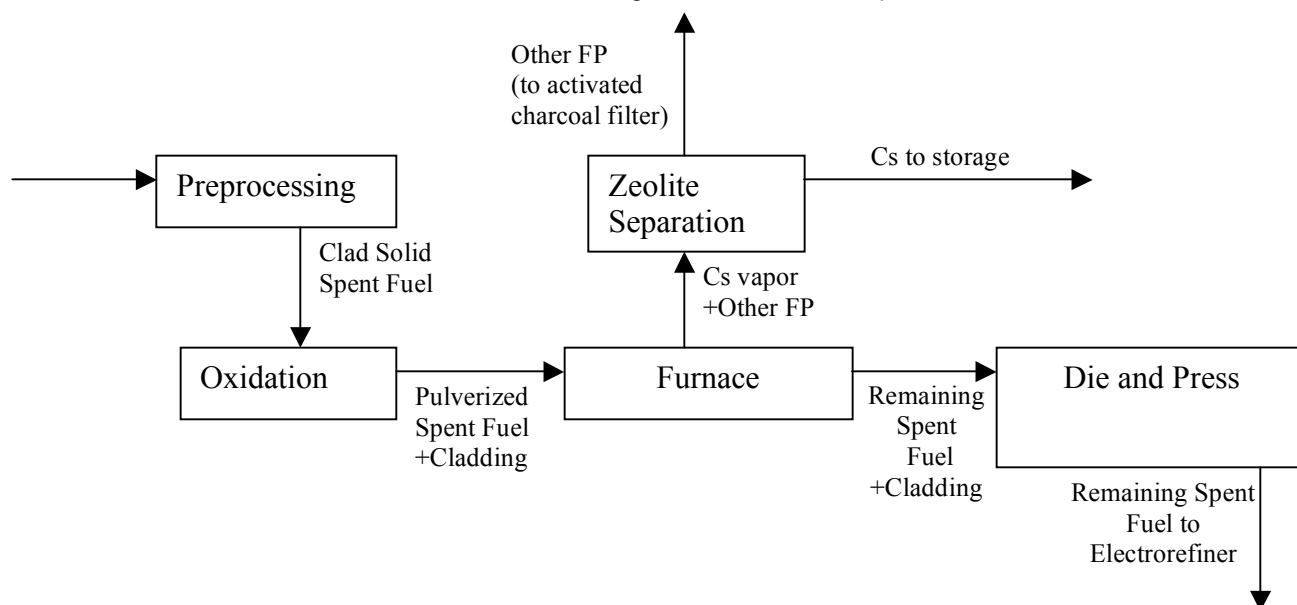
TABLE 2: Operating Cost Comparison/kg treated

	Zeolite	Cyclone
Pump	\$0.20	\$0.60
Furnace	\$0.07	\$0.07
Zeolite	\$0.20	\$0.00
Staffing	\$1.80	\$1.80
Total	\$2.27	\$2.47

4. Preliminary Bench Scale Design and Instrumentation

The final design is for a bench scale process that processes up to 500 g per batch. This size was selected since that is the size of the equipment used for the DEOX experiments [17]. The system consists of three main parts, a furnace in which the spent fuel is processed, a series of zeolites in which the cesium is removed from the off gasses and a pump to move the gas through the system. An overview of the design is presented in **FIGURE 10**.

FIGURE 10: Flow diagram of the selected process.



Since this is a bench scale design the remaining fuel should be analyzed for fission product removal, removal from cladding, and oxidization. Data based on the AIROX process gives ~90% removal from cladding [15]. The zeolite should also be analyzed to determine how much of which species were volatilized and at what rate they were released.

4.1 Furnace

Furnace design is the same as for the DEOX process [15]. The furnace is about 0.015 m³. A separate removal container fits inside the furnace. The inner container comes equipped with ports on the top for gas flow and instrumentation while also acting as the vessel into which the chopped fuel segments are placed. A 625 mesh screen made of a corrosion resistant material such as Incoloy®, prevents particles from leaving through the ports.

The instrumentation required is a flow controller for the incoming pressurized oxygen, a pressure sensor to monitor the pressure in the inner chamber, a temperature sensor to monitor the furnace temperature, and a power controller for the heater. A flow meter and control valve will be mounted on the gas inlet port to control the flow rate of O₂ into the system. A control valve and flow meter will also be mounted on the argon inlet valve. The furnace will be heated with standard electrical heating coil.

The furnace will operate in two stages. After it is loaded, the argon will be removed with the vacuum pump and the chamber will be filled with O₂ from a pressurized tank. The furnace is brought to 500-700°C for 2 hours. The pressure will be monitored and maintained at 1 atm. New O₂ will slowly enter and exit the system in order to preserve the excess oxygen. The O₂ supply will then be shut off and the vacuum pump will begin removing the oxygen. When the pressure becomes low enough to prevent backflow the argon inlet valve will be opened slightly to allow an argon atmosphere to replace the oxygen atmosphere. Once the oxygen atmosphere is gone the temperature can

be heated to about 950°C. Argon will flow through the system slowly, and a low pressure will be maintained in the system. The argon stream will run about 5 hours. The outgoing oxygen and argon stream will carry the fission products that have volatilized into the zeolite filtration system. From the oxygen stream it is expected that the following oxides will be present: Iodine oxide, rubidium oxide, and silver oxide. From the argon stream it is expected that the following additional oxides will be present: low amounts of oxygen (liberated from decomposing U_3O_8 and other oxides), tellurium, and molybdenum. Hopefully technetium and americium will not be volatilized.

4.2 Zeolite filtration system

The zeolite filtration system consists of three units in series. This number was chosen so that the temperature of the argon leaving the zeolite filtration system would be around 300 K (see **APPENDIX F**). The third stage should not accumulate cesium, but it is there to ensure that no cesium will enter the charcoal filter. Each unit contains 40 grams of zeolite contained in a stainless steel casing with a diameter of 2 cm and a length of 30 cm. The stainless steel casings are designed so that they can be permanently welded shut.

The zeolite filtration system requires a thermocouple to monitor the temperature at each stage and Geiger counters to give an estimate of the flow rates of radioactive materials.

In the preliminary calculations (see **APPENDIX B**), it was determined the maximum possible pressure drop across each zeolite separation unit was about 332 Pa. The lowest rank of the rotary compressor series with a compression capability of 140 kPa and a power requirement of 17.5 kW would work for the process. The pump will be located downstream of the dilute zeolite separation unit.

In the heat transfer computations (see **APPENDIX F**), it was also determined that a forced convection argon-gas cooling system is required to maintain the temperatures of each zeolite unit. The average temperatures of each of the three stages arranged in the order of nearest the furnace equal 910, 375, and 35°C, respectively.

Following the zeolite system there is an activated carbon filter that should trap any remaining radioactive species. There should be a Geiger counter on this as well to determine when things are entering the system.

4.3 Compression System for Particle Size Increase

In order to create compact rods from the resulting powder it is necessary to use a die and rod apparatus. This should probably be sized such that it can create rods of a size similar to incoming fuel rods (about 5cm length, 1cm diameter). That way it can also be used to create surrogate fuel rods for use in testing the process.

5. Economic Overview

5.1 Full Scale Economics

The total cost of operation was calculated by determining a good estimate of the operating cost of a reasonably sized reference system, linearly scaling it to the total amount of waste to be processed, and adding the fixed capital investment to the total operating cost.

The operating cost per kilogram was calculated by pricing a batch system designed to process one 20 kg batch every 8 hours (2 for oxidation, 5 for removal under argon, and 1 for loading and unloading). Since roughly 90 thousand tons are to be processed over the next thirty years [5], 330 kg needs to be processed per hour. Processing this amount will require 140 of the 20kg systems. The system was calculated to cost \$45 to operate per batch (**APPENDIX C**). This gives an operating cost of \$800 per hour, or \$2.30 per kilogram of waste processed. Over the thirty years required to process the fuel the overall operating cost would be about \$200 million.

The fixed capital investment was calculated by determining the overall equipment cost for the reference system, and assuming that it made up 28 percent of the overall fixed capital investment [24]. It is also important to consider the cost of hot cell space. The above system was estimated to require 85 square feet of space. Assuming that hot cell space will cost \$50,000 per square foot [25], the hot cell space would cost \$4.3 million for each batch unit. Since the above system had an equipment cost \$1 million (**APPENDIX C**) the entire system would cost around \$8 million. The overall fixed capital investment for 140 of the above systems, then, is \$1,100 million. It is important to note that this is an overestimate of the cost, since the economics will not scale linearly. All of these costs are laid out in **TABLE 3**.

TABLE 3: Cost of Reference System, Fixed Capital Investment and Operating Cost

(Costs are from Plant Design and Economics for Chemical Engineers)

Reference System

20kg capacity

8hrs processing time

Zeolite Separation

Equipment	Capital Cost	Operating Cost
25kw Compressor	\$6,000	\$8.10
Furnace (0.6m ³)	\$1,000	\$1.50
Press (7500cm ²)	\$1,000,000	\$3.00
Robotic Zeolite Bed Changing System	\$10,000(assumed)	
Zeolite (\$6.60/kg)		\$2.76
Operator Cost (\$30/hr)		\$30.00
Total	\$1,000,000	\$45.36
Hot Cell Space	\$4,250,000	
FCI	\$7,800,000	
Unit cost(1/kg/hr, 1/kg)	\$3,100,000	\$2.27
Overall Cost(350 kg/hr, 9*10 ¹⁰ kg)	\$1,100,000,000	\$200,000,000

5.2 Storage Economics

Low-level radioactive waste typically costs less than \$1000/ft³ for disposal, but in this case, the waste must be more spread out, as heat considerations are an issue, and the waste disposal site, if permanent, will need to be monitored for an extremely long period of time.

It is desirable that the temperatures inside of the individual storage units not exceed 300°C. Given the thermal conductivity of zeolite 4A and heat generated by the cesium oxide, the individual storage canisters, if stored under 10 feet of earth, should not have a critical dimension greater than 30 cm. If the waste is stored in 0.5 kg units, the units need to be spaced 2 m apart to facilitate natural cooling, assuming they are arranged in a hexagonal arrangement. If each unit is placed inside a reinforced concrete vault with 1 m thick walls, the total cost of each vault is \$750 (**APPENDIX D**). Assuming that these vaults comprise 45 percent of the total facility cost **[24]**, each unit would cost \$1700 to store. The total amount of cesium oxide produced (440 metric tons) would then cost about \$1,400 million to place in long-term storage.

The waste disposal site must then be monitored for environmental contamination, as well as to prevent trespassers from tampering with the waste. If \$5,000 million were saved in an annuity capable of earning 2% interest, after inflation, it would allow for a site operating cost of \$100 million per year in perpetuity. This money would be used to check on and repair vaults and zeolite modules, as well as securing the site and monitoring any environmental contamination of the site. The site would need to be monitored for 1200 years before it would be safe to stop monitoring the waste.

Permanent disposal will then cost around \$30,000 per kilogram of cesium waste, or \$70 per kilogram of spent fuel processed. Another option may be storing the cesium waste for around 60 years and then moving it into the long-term waste repository. That would not lower the disposal cost significantly, but would lower the risk of environmental contamination dramatically.

TABLE 4: Total Project Cost	
(millions of dollars)	
Fixed Capital Investment	\$1,100
Lifetime Operating Cost (30yrs)	\$200
Storage Cost	
Pre Op and Operational Expenses	\$1,400
Post Op Expenses	\$5,000
total cost	\$7,700

5.3 Overall Economics

The entire project will cost roughly \$7,700 million. It is important to note that this is a very rough, order of magnitude approximation. The project would nearly double the capacity of any long-term waste repository. The long-term waste repository is projected to cost \$43,000 million **[5]**, the bulk of this cost is transporting and handling waste, and it is unlikely to decrease when the Cs is removed. However, removing the

cesium would reduce the heat load on any long-term waste repository during its first couple hundred years of operation. This would simplify repository design and selection and decrease repository size.

6. Future Work:

In order to progress it is necessary to improve the available data, a more exhaustive literature search and experimental verifications are necessary before any large-scale implementation can be considered. The bench scale system presented in the Preliminary Bench Scale Design section can be used to calculate many of the necessary parameters, such as kinetics, exact molar flow rates for various estimated fuel types, and resulting particle sizes. Additionally, research into solving the particle size problem should be conducted as the current method presents serious financial, logistical, and operational problems.

7. List of Nomenclature

FP	Fission Products
TRU	Transuranic Elements

8. References

- [1] *Ullmann's Encyclopedia of Industrial Chemistry*. 5th rev. ed. **A17** "Nuclear Reactor Technology" (752-753). VCH: New York, New York. 1986.
- [2] Simpson, Michael. "Cs separation project." Personal email communication. Michael.simpson@anl.gov. 13 Nov. 2004.
- [3] Argonne National Laboratory Engineering Research online. "Electrorefiners." <http://www.era.anl.gov/spentfuel/refiner.html>. 21 Apr 2005.
- [4] Usami, Tuyoshi and Tetsuya Kato. "Development of Pyrochemical Reduction Process of Oxide Fuels to Metal." http://criepi.denken.or.jp/en/e_publication/a2001/01seika8.pdf
- [5] "Analysis of the Total System Life Cycle Cost of the Civilian Waste Management Program," DOE/RW-0533 May 2001
- [6] Karell, E.J. and K.V. Gourishankar. "Electrometallurgical Treatment of Oxide Spent Fuel—Engineering-Scale Development." *Proceedings of the American*
- [7] WebElementsTM Periodic table (professional edition)
<http://www.webelements.com/webelements/index.html>
- [8] Wilson, L.F. "Cesium Oxides and Hydroxide." *Supplement to Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry*. Vol. III, Suppl. II: The Alkali Metals, Part 2. Ed. J.W. Mellor. Longmans Green & Co. Ltd, London, England. 1963.
- [9] Simpson, Michael. "Re: Cesium Removal Project" Personal email communication. Michael.simpson@anl.gov. 12 Apr. 2004.
- [10] Gerow, I.H., J.E. Smith, Jr., M.W. Davis, Jr. "Extraction of Cs⁺ and Sr²⁺ from HNO₃ Solution Using Macrocyclic Polyesters." *Separation Science and Technology*. **16** (5) 519-548. 1981.
- [11] *Ullman's Encyclopedia of Industrial Chemistry*. 5th rev. ed. **A6** "Cesium and Cesium Compounds" (154). VCH: New York, NY. 1986.
- [12] *Encyclopedia of Chemical Reactions*. **II** (626-633). Reinhold Publishing Corporation, Maple Press: York, Pennsylvania. 1948.
- [13] *Encyclopedia of Chemical Technology*. **1** "Alkali Metals" (454). 1947.
- [14] Simpson, Mike. Idaho National Labs E-mail communication. "RE: Cs separation midterm update." 28 Mar. 2005.

- [15] Brand, G.E. and E.W. Murbach. "Pyrochemical Reprocessing of UO₂ by AIROX Summary Report." NAA-SR-11389. 31 Aug 1965. *Nuclear Society, Third Topical Meeting on DOE Spent Nuclear Fuel and Fissile Materials Management*. Charleston, South Carolina, 1998.
- [16] Westphal, B.R., et al. "Initial Testing of the DEOX Process at ANL-W." *Transactions of the American Nuclear Society*. June 13-17, 2004. 84-85.
- [17] Bateman, K.J, B.R. Westphal, and M.A. Stawicki. "Experimental Equipment Design and Testing of the DEOX Process." *Proceedings of ICONE12: 12th Int'l Conference on Nuclear Engineering*. April 25-29, 2004. Arlington, VA.
- [18] Hoyt, R.C., L.F. Grantham, R.G. Clark, and P.W. Twichell. "AIROX Dry Reprocessing of Uranium Oxide Fuels." ESG-DOE-13276. 12 Jul 1979.
- [19] Thermcraft, Inc. online. "Fibercraft Full Cylinder Heaters 1100C (2012F) – Helically wound wire." <http://www.thermcraftinc.com/pdfs/vf360.PDF>. 21 Apr 2005.
- [20] M. N. Rahaman "Ceramic Processing and Sintering" 2nd edition, Marcel Dekkar Inc. New York. 2003.
- [21] Arterburn, R.A. "The Sizing and Selection of Hydrocyclones." Krebs Engineers online, 2005. http://www.krebs.com/documents/83_sizing_select_cyclones.pdf
- [22] Peacock, H.B., T.M. Adams, A.J. Duncan, N.C. Iyer. "Melt-Dilute Treatment of Spent Nuclear Fuel Assemblies from Research and Test Reactors," WSRC-MS-99-00751.
- [23] Heo and Seff. "Cesium Vapor Reacts with K⁺-Exchanged Zeolite A to Give Fully Cs⁺-Exchanged Zeolite A Containing (Cs₄)⁺³ Clusters." *Perspectives in Molecular Sieve Science: ACS Symposium Series 368*. Eds. Flank, W.H. and T.E. Whyte, Jr. American Chemical Society, Washington DC. 1988. 177-193.
- [24] Peters, Timmerhaus, and West. *Plant Design and Economics for Chemical Engineers*. 5th Ed. McGraw-Hill, New York. 2003. 826.
- [25] Simpson, M. "RE: Last Minute Cesium Details..." Personal email communication. Michael.simpson@anl.gov. 20 Apr 2005.

Appendix A: Federal Health and Environmental Safety Regulations

Although the overall process involves handling radioactive wastes within sealed and quarantined hot cell space, the health and welfare of people and the environment remains a very high priority. Federal regulations that help ensure the safety of workers in the facility and the public will be adhered to at all times during the effect of this process.

The exact laws and guidelines on the storage of the final high-level waste products from this process as dictated by the Nuclear Regulatory Commission (NRC) and Environmental Protection Agency (EPA) are quite comprehensive and exhaustive, beyond the scope of this design consideration. However, in the midst of many regulations, there are some general principles that must be addressed in how the waste should be stored in an environmentally safe manner. First, the releases of radionuclides from the repository must be less than figures specified by the EPA; a common example equals about 100 Ci/(kton of waste processed). Also, the final waste products must be placed at least 300 meters beneath Earth's surface and in an arid region of low water content with a groundwater travel time greater than 10,000 years but not less than 1000 years. Furthermore, waste must be kept far away from natural resource areas and the populated vicinities. The ground at that location must also exhibit very low geological activity (i.e., no earthquakes or volcanic activity). The more exact details on handling high level waste in this process is outlined in Regulation 40CFR191 [A1].

The more probable source of concern for this process is the safety of those actually working on the process. The International Atomic Energy Agency (IAEA) has provided three main guidelines that must be addressed in any safety consideration of nuclear wastes or the processes involving them:

1. Establish and maintain an effective defense against radiological hazard.
2. Keep the potential release of radioactive material from the plant as low as reasonably achievable (ALARA) and below predefined limits. The definition of ALARA limits for radionuclides are outlined in EPA Regulations 10CFR835 and 40CFR61 [A1], which will be adhered to. The maximum annual exposure limit of radiation among workers is 0.05 sieverts/year [A2].
3. Prevent accidents and make sure the likelihood of accidents with severe radiological consequences is infinitesimally small. Worker safety is specified in Regulation 29CFR1910.

One of the ways in which these guidelines are addressed is in the construction of the appropriate hot cell space, the concentric barriers of which are typically referred to as the "defense-in-depth" construction that will inevitably apply in this design case. The construction standards are specified by the Occupational Safety and Health Act (OSHA) Regulation 29CFR1926 [A3].

In all steps of the process (including the final waste storage facility), highly sensitive radiation monitors will continuously be online and located in several locations

so as to detect leaks of radiation. In case of such an event, the defect must be corrected immediately and emergency response must take effect. The emergency procedures and training are outlined in EPA Regulations 40CFR355 and 40CFR370.

[A1] United States Environmental Protection Agency. [Http://www.epa.gov](http://www.epa.gov). 20 Apr 2005.

[A2] Encyclopedia of Chemical Technology. **17** “Nuclear Reactors (Waste Management) and Nuclear Reactors (Safety).” 471-476, 481-483, 494-500.

[A3] US Government Printing online. [Http://www.access.gpo.gov](http://www.access.gpo.gov). 20 Apr 2005.

Appendix B: Zeolite Pressure Drop Calculations

*Assumptions: incoming gas stream mostly Ar (use density and viscosity of Ar)
density of Ar is a function of the ideal gas equation

Ar gas through zeolite modeled as gas passing through a packed bed of solid catalyst particles.

Zeolite properties:

D_p/m	ϕ_s , Perry's	$\phi_{porosity}$	$SA/(m^2/kg)$
1.50E-03	0.83	0.3	7
$\rho/(kg/m^3)$	L/m	D_{nom}/m	A/m^2
690	0.3	0.2	3.14E-02

Ar properties:

$T/^\circ C$	$\mu/(Pa\cdot s)$	$\rho/(kg/m^3)$	$G/(kg/(m^2\cdot s))$	m^3/s
1000	3.90E-05	0.04	2.98E-04	2.44E-04
0	1.95E-05	1.78	1.39E-02	2.44E-04

Ergun equation				
$T/^\circ C$	refresh time/s	mass flow	$\Delta P/Pa$	total pressure drop/Pa
1000	900	9.36E-06	110.65	331.96
0	900	4.36E-04	56.30	168.90

= torr
2.49
1.27

Ergun Equation:

$$\Delta P = - \frac{G \Delta z}{\rho g_c D_p} \left(\frac{1 - \phi}{\phi^3} \right) \left[\frac{150(1 - \phi)\mu}{D_p} + 1.75G \right]$$

- ΔP Pressure drop (Pa)
- ϕ porosity
- g_c gravitational conversion factor
- D_p particle diameter in the bed (m)
- μ gas viscosity (Pa-s)
- Δz length of bed (m)
- u superficial velocity (m/s)
- ρ gas density (kg/m^3)
- $G = \rho u$ superficial mass velocity ($kg/(m^2\cdot s)$)

Reference:

Fogler, H.S. *Elements of Chemical Reaction Engineering*. 3rd ed. Prentice Hall, New Jersey: 1999. 154

Appendix C.1: Cost of Reference System, Fixed Capital Investment and Operating Cost

(Costs are from Plant Design and Economics for Chemical Engineers)

Reference System

20kg capacity

8hrs processing time

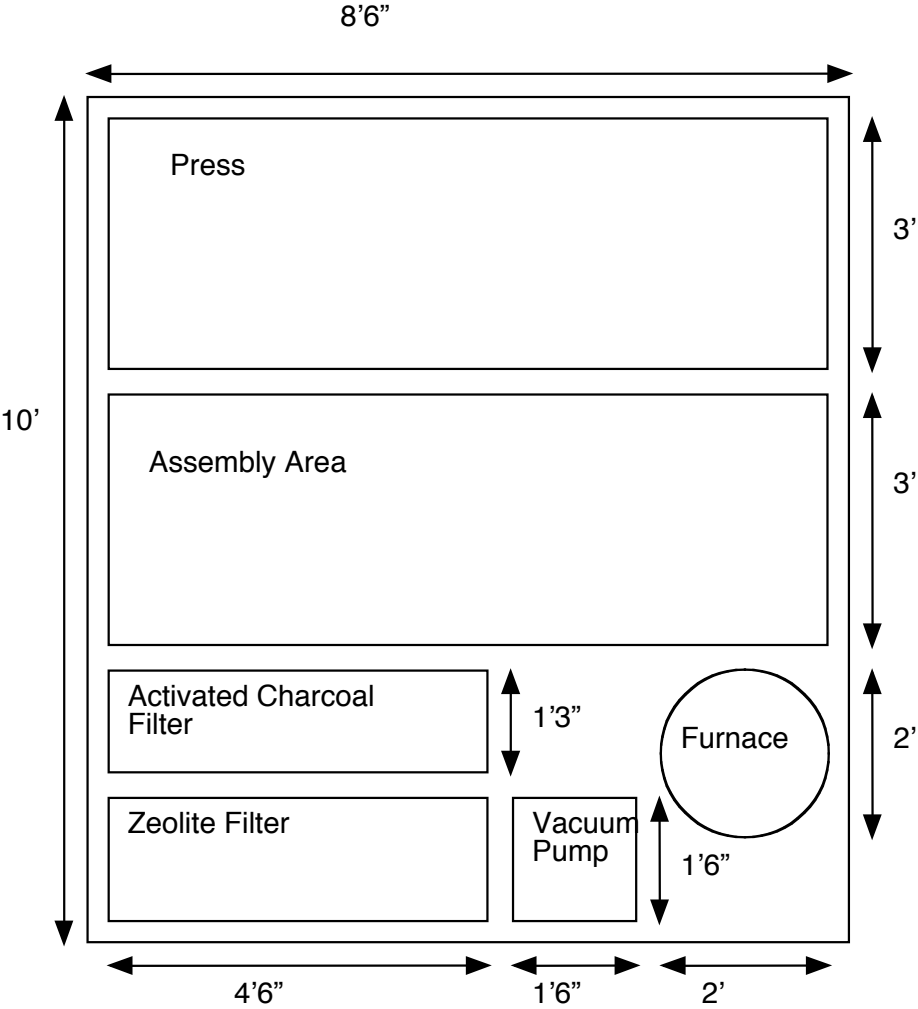
Zeolite Separation

Equipment	Capital Cost	Operating Cost
25kw Compressor	\$6,000[24]	\$8.10[24]
Furnace (0.6m ³)	\$1,000[24]	\$1.50[24]
Press (7500cm ²)	\$1,000,000(assumed)	\$3.00(assumed)
Robotic Zeolite Bed Changing System	\$10,000(assumed)	
Zeolite (\$6.60/kg)		\$2.76[14]
Operator Cost (\$30/hr)		\$30.00[24]
Total	\$1,000,000	\$45.36
Hot Cell Space	\$4,250,000[25]	
FCI	\$7,800,000	
Unit cost(1/kg/hr, 1/kg)	\$3,100,000	\$2.27
Overall Cost(350 kg/hr, 9*10 ¹⁰ kg)	\$1,100,000,000	\$200,000,000

Cyclone Separation

Equipment	capital Cost	Operating Cost
45kw Compressor	\$18,000[24]	\$14.90[24]
Furnace (0.6m ³)	\$1,000[24]	\$1.50[24]
Press (7500cm ²)	\$1,000,000(assumed)	\$3.00(assumed)
Cyclone	\$5,000[21]	
Operator Cost (\$30/hr)		\$30.00[24]
Total	\$1,000,000	\$49.40
Hot Cell Space	\$4,250,000[25]	
FCI	\$7,900,000	
Unit cost(1/kg/hr, 1/kg)	\$3,200,000	\$2.47
Overall Cost(350 kg/hr, 9*10 ¹⁰ kg)	\$1,100,000,000	\$222,000,000

Appendix C.2: Equipment Sizing Layout Within 85 ft² Hot Cell Area



Appendix D: Storage Costs

Each container can hold 0.5kg Cs, 880,000 units are needed

Cost of concrete cask	unit cost	units			cost
Concrete Cost:	\$70.00[24]	1/cu yd	volume	10 cu yd	\$700.00
Reinforcement Cost	\$0.10[24]	1/sq ft	surface	250 sq ft	\$25.00
Gravel Cost	\$12.00[24]	1/cu yd	base	0.5 cu yd	\$6.00
Grating Cost	\$45.00[24]	1/hr	time	0.033 hr	\$1.50
Total					\$730.00
FCI					\$1,620.00
FCI/processed kilogram					\$15.60
FCI total					\$1,400,000,000

Appendix E: Overall Mass Balance on System (for 1 kg of processed fuel)

	Input[1] (g)	Output (g) (calculated from melting points listed in Appendix H)				Balance
	Spent Fuel	Spent Fuel	Zeolite	Activated Charcoal	Filters	
Cladding	100	100				0.0
Molybdenum	3.5		3.5			0.0
Palladium	1.4	0.7	0.7			0.0
Silver	0.1		0.1			0.0
Cesium	2.3		2.3			0.0
Tellurium	0.5	0.2	0.3			0.0
Rubidium	0.4		0.4			0.0
Iodine	0.2		0.0	0.2		0.0
Uranium	960.9	960.9				0.0
Others	30.7	30.7				0.0
Total	1100	1092.5	7.2	0.2	0	0.0

Appendix F: Zeolite Temperature Calculations

Argon Properties				
Mass Flow Rate	9.36E-06	kg/sec		
Specific Heat Capacity	520	J/kg*k		$Re_L = Lv\rho/\mu$
Viscosity	2.08E-05	Pa*s		$Pr = \frac{\mu C_p}{k}$
Thermal Conductivity	0.018	W/m*K		$Nu_D = \frac{hD}{k}$
Temperature	300	K		
Pr	0.610			
ρ	1.784	kg/m ³		
Module Properties				
Module Diameter	0.2	m		$Nu_L = .036 Re_L^{4/5} Pr^{1/3}$
Module Length	0.3	m		$Re_L > 10^6$
Module Surface Area	0.188	m ²		
Thickness	0.001	m		
Thermal Conductivity	18	W/m*K		
Cross Sectional Area	6.28E-04	m ² €		
Heat Transfer Rate	1.13E-02	W*m/K		
Heat Generation (stage1)	875	W (max)		
Heat Generation (Stage 2)	438	W		
Heat Generatin (Stage 3+)	0	W		
Coolant Velocity	0.5	m/s		
Re _L	1.29E+04			
Nu _L	59.2			
h	5.25	W/m ² *K		
	stage 1	stage 2	stage 3	
Entering Temperature	1300	1076	502	K
Exiting Temperature	1076	502	300	K
Average Temperature	1184	753	309	K
ΔT	884	453	9	K
Heat Transfer to Argon Atmosphere	874	447	9	W
Heat Flow Into Stage	6	5	2	W
Heat Flow Out of Stage	5	2	1	W
Heat Generation in stage	875	438	0	W
Conductive Transfer into Stage	13	15	8	W
Counductive Transfer out of stage	15	8	0	W
balance	0.0	0.0	0.0	W

Appendix G: Melting Points and Boiling Points of Spent Fuel Oxides^[7]

Element	Symbol	Oxide	Oxide MP	Oxide BP
neodymium	Nd	Nd ₂ O ₃	2270	4118
cerium	Ce	CeO ₂	2500	
lanthanum	La	La ₂ O ₃	2305	4200
praseodymium	Pr	Pr ₂ O ₃	2300	
samarium	Sm	Sm ₂ O ₃	2335	
yttrium	Y	Y ₂ O ₃	2439	4300
gadolinium	Gd	Gd ₂ O ₃	2420	
dysprosium	Dy	Dy ₂ O ₃	2408	
uranium	U	UO ₂	2827	
plutonium	Pu	PuO ₂	2400	2800
americium	Am	AmO ₂	1000	(decomposes)
neptunium	Np	NpO ₂ ?		
curium	Cm	CmO ₂ ?		
zirconium	Zr	ZrO ₂	2677	
molybdenum	Mo	MoO ₃	795	1155
ruthenium	Ru	RuO ₂	1200	(sublimes @MP)
technetium	Tc	TcO ₂	1000	(sublimes @MP)
palladium	Pd	PdO	750	(decomposes)
rhodium	Rh	RhO ₂ ?		
cadmium	Cd	CdO	1500?	1559
silver	Ag	Ag ₂ O	460	
cesium	Cs	Cs ₂ O	490	(decomposes)
barium	Ba	BaO	1913	2000
strontium	Sr	SrO	2530	3000
tellurium	Te	TeO ₂	733	1245
rubidium	Rb	RbO ₂	432	
iodine	I	I ₂ O ₅	300	(decomposes)
europium	Eu	Eu ₂ O ₃	2350	