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Applications of stable isotopes in medicine are becoming more widespread. This has resulted from the increased availability and reduced cost of these isotopes and the improved reliability and sensitivity of detection techniques such as carbon-13 nuclear magnetic resonance. Isotopes are used in compounds labeled with either the stable isotope itself, such as carbon-13 and oxygen-18, or with the radioactive isotope that can be produced by irradiating the stable isotope, such

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as the irradiation of xenon-124 to produce iodine-125. As the demand for stable isotopes increases, larger scale production facilities will be justifiable. The increased size of production facilities should result in yet lower unit selling prices.

A large number of methods has been suggested for the separation of stable isotopes. This paper concerns itself with four methods which have proven extremely useful for the separation of the isotopes of low and medium atomic weight elements. The four processes discussed are gas phase thermal diffusion, liquid phase thermal diffusion, chemical exchange, and distillation.

GAS THERMAL DIFFUSION

Gas thermal diffusion has been used to enrich the isotopes of the noble gases and carbon for several years. Table I shows the progress that has been made in separating these isotopes. These separations have been carried out in variously designed thermal diffusion columns. Convection currents in the thermogravitational thermal diffusion columns multiply the relatively small basic thermal diffusion separation factor. However, in almost all cases several columns must be connected to each other to obtain the desired separation.

Mound Laboratory uses two types of thermal diffusion

columns. The first type is the "hot wire" column which is the original type column used at Mound Laboratory. A schematic of this type column is shown in Fig. 1. These columns are so named because the hot wall is a wire (normally 0.16 cm in diameter) heated by direct current. This wire is held in the proper axial position by fingers protruding from the outer cold wall of the column and by tension placed on the wire by weights at the bottom of the column. These original columns have been almost completely replaced with concentric cylinder columns in which the hot wall is a tubular heater (normally 0.8 cm in diameter).[1] A schematic of this column is shown in Fig. 2. These concentric columns are easier to fabricate and more reliable because of their simpler design. Precise axial alignment of the heater with respect to the cold wall is obtained with spacers which are slipped over the heater and then spot welded to the heater at 40-cm intervals. Nineteen of these columns, each 4.9 m high, are located in a common water jacket. The columns are then connected in various series-parallel configurations to form, by means of piping and valves, what is called a cascade of columns. Specially designed magnetically driven vane pumps are used to circulate the gas between columns.

The number of columns placed in parallel and in series

in each cascade depends on the particular separation task for which the cascade is to be used. Mound Laboratory has developed computer programs which simulate both the steady-state and transient performance of these thermal diffusion cascades. These computer programs are used to determine the optimum arrangement of the columns for each separation. For example, Fig. 3 shows the column arrangement to enrich xenon-124 from its natural abundance of 0.096% to 20% xenon-124. This 19-column thermal diffusion cascade produces 10 cm^3/day of xenon containing greater than 20% xenon-124. A similar cascade arrangement can also be used to obtain 1% xenon-124 which contains greater than 60% xenon-129. Another 19-column cascade has been used to produce krypton with the krypton-78 enriched to greater than 50%.

Enrichments of the middle isotopes of a given element can be obtained by combining several cascades together. An example is the arrangement of three cascades shown in Fig. 4. The first cascade produces a 99% krypton-86 product stream and a stream depleted in krypton-86. The top stream depleted in krypton-86 is fed to the second cascade. Ninety percent krypton-84 can be obtained from the bottom of this second cascade since most of the krypton-86 was stripped out in the

first cascade. This second cascade also produces a stream depleted in both krypton-86 and krypton-84 which is fed to the third cascade to produce 70% krypton-82 and 70% krypton-83.

The middle isotopes of xenon can be separated in an analogous manner.

LIQUID THERMAL DIFFUSION

Liquid mixtures as well as gases undergo a slight demixing in the presence of a temperature gradient, and the principle of the thermogravitational column can be used to create practical scale separation of isotopes in the liquid phase. For both liquid and gas phases the elementary separation effect is characterized by the thermal diffusion factor α_T as indicated in Fig. 5. The elementary effect is quite small. For the separation of sulfur-34 from sulfur-32 in carbon disulfide it amounts to a 1% change in the isotope ratio for a temperature difference of 100°C; however, in a properly constructed thermogravitational thermal diffusion column this small effect can be multiplied several hundredfold.

The possibility of separating isotopes in the liquid thermal diffusion column has been known for many years. A large-scale plant based on this technique was constructed and operated by the United States during World War II for the purpose of separating uranium isotopes in the form of liquid UF_6.[2] The uranium isotope separation process was technically successful but economically unsound for large-scale operations. Since it was dismantled in 1945, little attention has been given to isotope separation by this method. The potential application of liquid thermal diffusion to the separation of isotopes on a small scale was discussed by K. F. Alexander in a comprehensive review paper published in 1960.[3]

Although the process is economically impractical for large-scale operations, it has certain attractive advantages for the separation of gram and perhaps even kilogram quantities of a number of isotopes. These include the following: 1) Large separations can be obtained in relatively small, short columns. 2) The same type apparatus can be applied to enrich isotopes of any element which has a suitable liquid compound. 3) The separation can be accomplished at relatively low temperatures.

A comparison between liquid and gas phase thermal diffusion

is shown in Fig. 6. From the relatively limited amount of work that has been reported, it appears that the basic effect in liquids is relatively much larger than it is in gases. For a given percentage mass difference, the effect in liquids is about 3 to 5 times larger than in the gas phase. The size of liquid thermal diffusion columns is correspondingly smaller. Practical liquid columns have a much smaller spacing between the hot and cold walls, and temperature differences between hot and cold walls are typically much less.

An effort has been under way at Mound Laboratory for several years to develop liquid thermal diffusion as a tool for practical scale separation of isotopes. A 60-cm research column was constructed to develop experimental techniques, to study the relationship between column behavior and theory, and to derive information regarding the magnitude of the thermal diffusion factor for several systems. The results from work with this short column have been highly encouraging. For most conditions it was found that the behavior of the column could be adequately predicted from theory, and it was possible to obtain thermal diffusion factors for several compounds. These included isotopic pairs involving the elements hydrogen, carbon, chlorine, bromine, and sulfur. The results, which are being

prepared for publication elsewhere, indicate that the method is indeed feasible for small-scale separations.

Sulfur isotope separation with the 60-cm column is illustrated in Fig. 7. Carbon disulfide of natural isotopic abundance was circulated across the top of the experimental column. After a period of several days, the abundance of sulfur-34 in the bottom of the column increased to more than 11%. Over a period of time several grams of this enriched material were collected.

A prototype production cascade of nine liquid thermal diffusion columns is now being constructed at Mound Laboratory for separating sulfur, chlorine, and bromine isotopes at high enrichment. The prototype columns, which are 240-cm long, will be used alternately to separate sulfur-34, chlorine-35 and 37, and bromine-79 and 81.

At the present time some difficulty has been encountered in scaling the columns up from the 60-cm research design to the 240-cm prototype. The several columns constructed so far have not reached more than 10 to 40% of the theoretically expected performance. The discrepancy appears to be related

to the problem of maintaining a precisely defined spacing of approximately 250 μm between the hot and cold walls of the column over the longer length. Several alternate approaches are being evaluated, and it is expected that this problem will be solved shortly.

CHEMICAL EXCHANGE

Mound Laboratory is also investigating several chemical exchange processes for the enrichment of stable isotopes. These processes are based upon the fact that when certain compounds come in contact with each other, an isotopic exchange reaction takes place such that the lower molecular weight isotopes preferentially tend to reside in the chemical form of one of the reactants. In practical separations each reactant exists in a different phase so that the lighter isotope is preferentially enriched in one phase. Both gas-liquid and liquid-liquid chemical exchange systems are being studied at Mound Laboratory. Isotopes of medical interest which may be enriched by chemical exchange methods include the isotopes of carbon, nitrogen, sulfur, and various metal isotopes.

For several years Mound Laboratory has operated a five-column CO_2-carbamate chemical exchange system[4] to enrich

carbon-13 to greater than 90%.[5] As a result of data collected from the operation of this system, it is the authors' opinion that carbon monoxide distillation is a better process for the enrichment of carbon-13 at production rates in excess of 500 grams/year. Mound Laboratory has, therefore, discontinued the use of chemical exchange to produce enriched carbon-13 and is using distillation to enrich carbon-13 from natural abundance to 90%. The current status of carbon-13 distillation will be discussed in more detail later in this paper.

Mound plans to convert the five-column CO_2-carbamate chemical exchange equipment to the SO_2-$NaHSO_3$ chemical exchange system for the enrichment of sulfur isotopes. Development work on this sulfur enrichment process has recently been carried out in Germany[6] and Russia.[7] This system is normally refluxed by adding sodium hydroxide and sulfuric acid at the top and bottom reflux systems, respectively. Sodium bisulfate is withdrawn as a waste material from the refluxing operation. Open chemical reflux systems of this kind require and generate large amounts of chemicals and are, therefore, more complicated and expensive to operate. Mound has decided to convert the waste sodium bisulfate, by means of an electrodialysis unit, into the two reagents (sodium hydroxide and sulfuric acid)

necessary to close the reflux system. A schematic showing how this closed reflux system will operate is presented in Fig. 8.

When the conversion from carbon to sulfur is completed, the five-column chemical exchange system is expected to produce slightly over 1 kg of sulfur containing 90% sulfur-34. This stream, after chemical conversion, can also be fed to a liquid thermal diffusion system for enrichment of the sulfur-33 to much higher concentrations.

Mound Laboratory is also developing a new liquid-liquid chemical exchange process for the enrichment of the isotopes of various metals. The isotopes of several metals are currently enriched using the electromagnetic separations at Oak Ridge National Laboratory.[8] Initially, this chemical exchange work is being aimed at developing a calcium isotope enrichment process.

This new chemical exchange system consists of contacting an aqueous calcium salt solution with a ligand dissolved in an organic solvent. The ligand which has been primarily used is the calcium complex of the polyether dicyclohexyl 18-crown-6. [9,10]. A schematic of this polyether is presented in Fig. 9.

The isotopic exchange reaction can be written as follows:

$$^{40}Ca^{++}{}_{(aq)} + {}^{44}Ca^{++}\ \text{Complex}_{(org)} \rightleftarrows {}^{44}Ca^{++}{}_{(aq)} + {}^{40}Ca^{++}\ \text{Complex}_{(org)}$$

The single stage equilibrium separation factor for this reaction has been found to be approximately 1.004 for the calcium-44/calcium-40 separation. The half life of the exchange reaction is sufficiently fast so that the process is not expected to be reaction rate limited. The details of this development work are being prepared for publication elsewhere. A scientifically feasible reflux system has been worked out for this system. The phase reversal at the bottom of the liquid-liquid contactor is accomplished by the following reaction:

$$Ca\ L\ Cl_2{}_{(org)} + H_2O \rightarrow L_{(org)} + Ca\ Cl_2{}_{(aq)}$$

where L = dicyclohexyl 18-crown-6. The reflux reaction at the top of the system is

$$L_{(org)} + CaCl_2{}_{(aq)} \rightarrow CaLCl_2{}_{(org)}$$

Preliminary calculations indicate that a 20-column chemical exchange system could produce approximately 5 grams of calcium per day containing 10% calcium-48, 0.11% calcium-46, and 46% calcium-44. These partial enrichments may be useful for certain

medical applications. This material can also be used as feed material to the Oak Ridge National Laboratory electromagnetic separators (calutrons). This combined enrichment method should reduce the unit cost of highly enriched calcium-48 by at least a factor of 10 since the throughput of the calutrons is approximately proportional to the concentration of the isotope in the feed material.

It is believed that this liquid-liquid chemical exchange process can be successfully applied to the enrichment of the isotopes of the several other metals such as potassium, magnesium, mercury, and iron.

DISTILLATION

Distillation has been used to separate the isotopes of carbon, oxygen, nitrogen, and hydrogen. Carbon isotope enrichment is carried out by the cryogenic distillation of carbon monoxide. The cryogenic distillation of carbon monoxide is currently the best process for carbon isotope enrichment at production rates greater than 500 grams per year.[11]

Mound Laboratory is operating a two-column system which has a production capability of approximately 1 kilogram of

carbon-13 per year at an enrichment of 90%. This two-column system is also used to produce 20% carbon-13 and carbon-12 enriched to greater than 99.95% since these materials are also of interest for particular applications. Los Alamos Scientific Laboratory (LASL) is also using carbon monoxide distillation to produce several kilograms of carbon-13 and carbon-12.[12] Mound Laboratory is the sole USAEC distributor for enriched carbon isotopes. Carbon isotopes are available from Mound in the following basic chemical forms: carbon monoxide, carbon dioxide, barium carbonate, methane, and elemental carbon. These basic compounds can be synthesized into more complex labeled compounds by any of several privately owned companies or by the user himself.

The USAEC also enriches the isotopes of nitrogen and oxygen at LASL by the cryogenic distillation of nitric oxide. LASL is in the process of expanding its distillation facility for the production of the isotopes of carbon, oxygen, and nitrogen.[13]

SUMMARY

Both old and new methods are being applied to the enrichment of stable isotopes. Gas phase thermal diffusion will

continue to be used to enrich the isotopes of the noble gases (He, Ne, Ar, Kr, and Xe). Liquid phase thermal diffusion is being developed for the separation of the isotopes of chlorine, bromine, and sulfur. Chemical exchange will be used to enrich sulfur isotopes and is being developed for the enrichment of various metal isotopes such as calcium, and distillation will continue to be used for the separation of the isotopes of carbon, oxygen, and nitrogen. Development of these and other separation methods will be continued to provide enriched isotopes at their lowest unit cost.

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TABLE AND FIGURE CAPTIONS

Table I - Stable isotope enrichment by gas phase thermal diffusion

Figure 1 - Hot-wire gas phase thermal diffusion column

Figure 2 - Concentric cylinder gas phase thermal diffusion column

Figure 3 - Nineteen-column thermal diffusion system for enrichment of xenon-124 to 20%

Figure 4 - Operation of three thermal diffusion cascades for enrichment of krypton isotopes

Figure 5 - Basic liquid thermal diffusion separation effect

Figure 6 - Comparison of liquid and gas phase thermal diffusion columns

Figure 7 - Enrichment of sulfur isotopes by liquid thermal diffusion

Figure 8 - Sulfur isotope enrichment by SO_2-$NaHSO_3$ chemical exchange with closed reflux

Figure 9 - Configuration of the macrocyclic polyether dicyclohexyl 18-crown-6, $C_{20}H_{36}O_6$

TABLE I

STABLE ISOTOPE ENRICHMENT BY GAS PHASE THERMAL DIFFUSION

Year	Isotope	% Purity
1939	Chlorine-35	99.4
1939	Chlorine-37	99.6
1942	Krypton-84	98.3
1942	Krypton-86	99.5
1950	Neon-20	99.95
1950	Nitrogen-15	99.8
1953	Carbon-13	99.8
1955	Xenon-136	99.0
1956	Neon-21	99.6
1959	Oxygen-18	99.7
1959	Argon-38	99.98
1960	Neon-22	99.92
1962	Argon-36	99.99
1968	Oxygen-16	99.98
1971	Xenon-131	60
1971	Argon-40	99.98
1972	Xenon-124	60
1972	Krypton-78	50
1973	Krypton-82	70
1973	Krypton-83	70
1973	Xenon-129	80

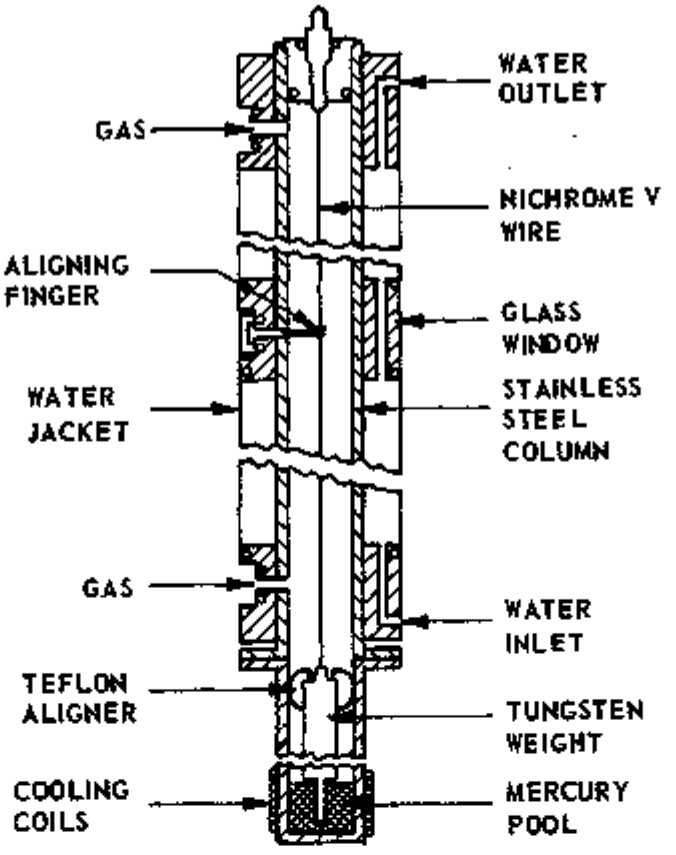


FIGURE 1 - Hot-wire gas phase thermal diffusion column.

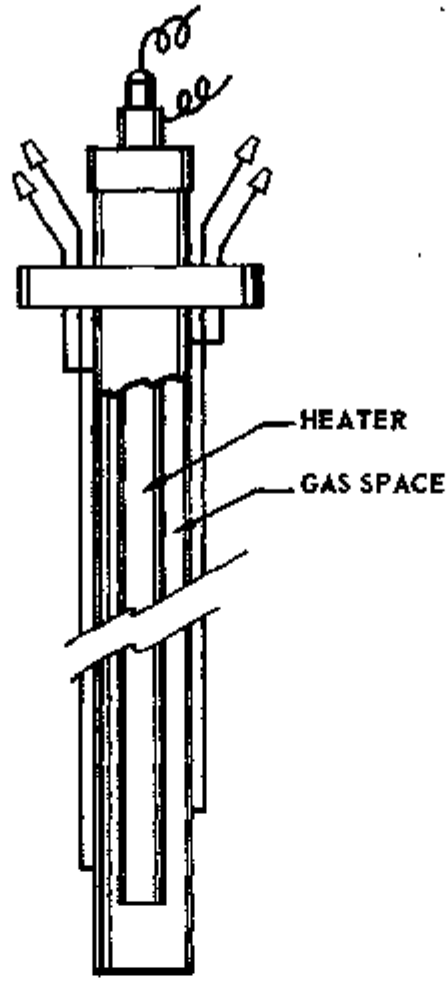
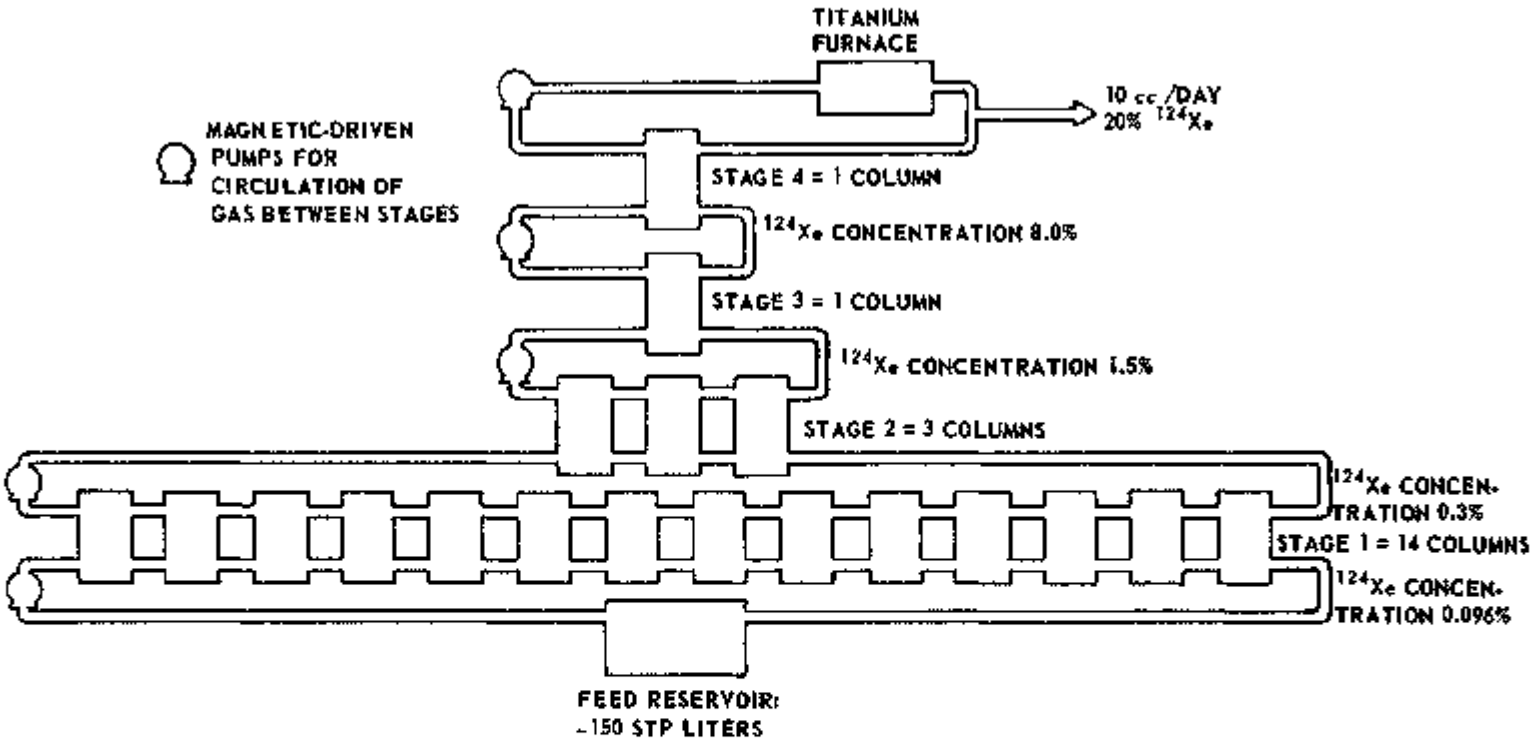


FIGURE 2 - Concentric cylinder gas phase thermal diffusion column.



NATURAL ABUNDANCE XENON

XENON-124	0.096%
XENON-126	0.090%
XENON-128	1.92 %
XENON-129	26.44 %
XENON-130	4.08 %
XENON-131	21.18 %
XENON-132	26.89 %
XENON-134	10.44 %
XENON-136	8.87 %

FIGURE 3 - Nineteen-column thermal diffusion system for enrichment of xenon-124 to 20%.

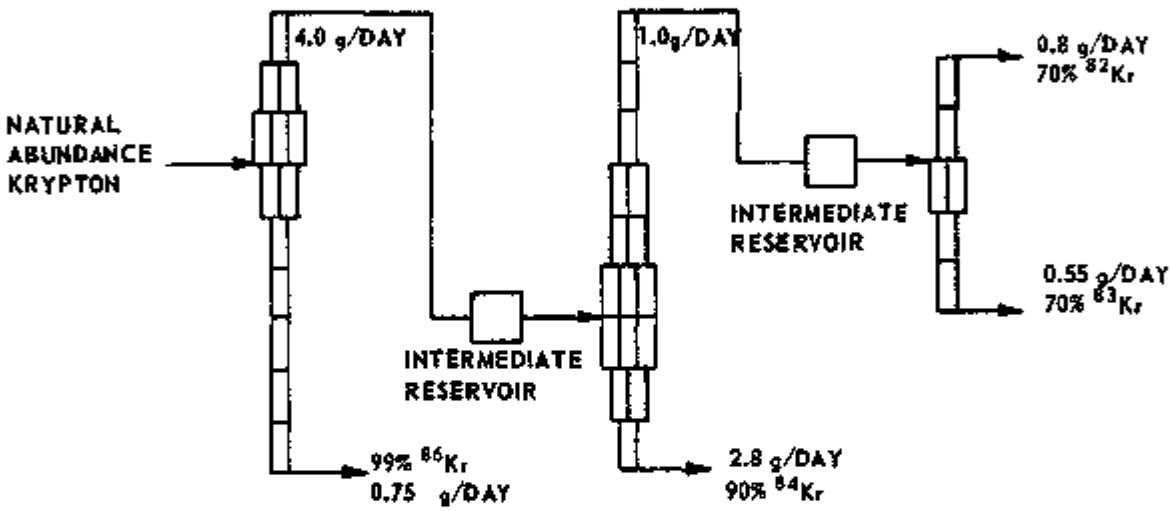


FIGURE 4 - Operation of three thermal diffusion cascades for enrichment of krypton isotopes.

$$q = \frac{C_H}{C_c}\frac{(1-C_c)}{(1-C_H)} = \left(\frac{T_H}{T_c}\right)^{\alpha_T}$$

$q = 1.010$

for $C^{32}S^{32}S$ - $C^{34}S^{32}S$

at 100°C TEMP. DIFFERENCE

FIGURE 5 - Basic liquid thermal diffusion separation effect.

	GAS	LIQUID
α_T	<.5Δ m/m	1.5Δ m/m
ΔT	700°K	100°K
T	300-800°K	300-400°K
GAP	3-12 mm	0.2-0.3 mm
HEAT SOURCE	ELECTRICAL	STEAM

FIGURE 6 - Comparison of liquid and gas phase thermal diffusion columns.

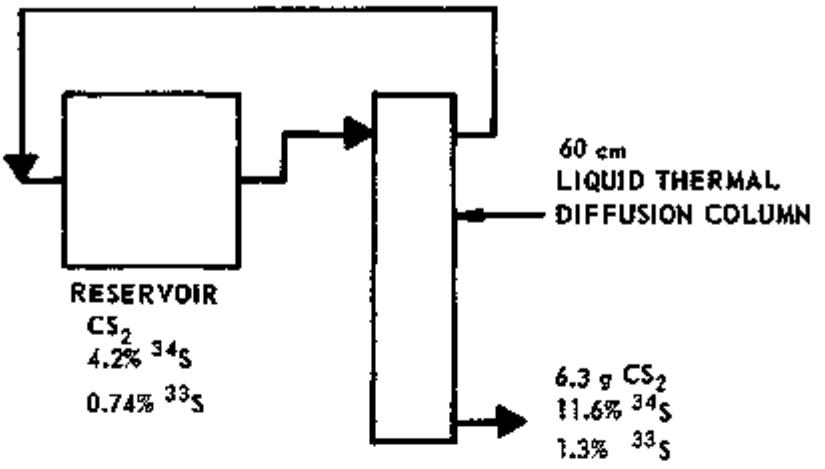


FIGURE 7 - Enrichment of sulfur isotopes by liquid thermal diffusion.

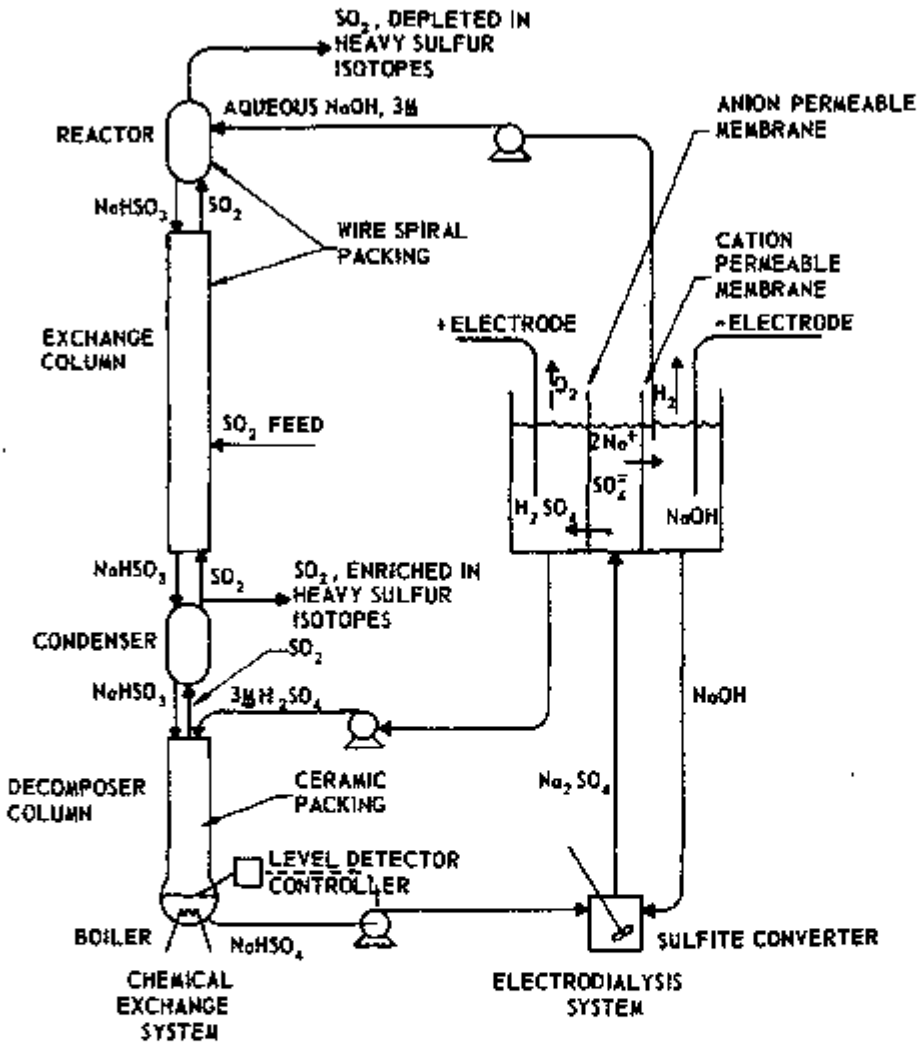
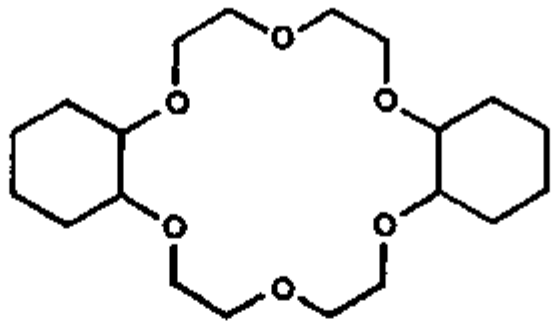


FIGURE 8 - Sulfur isotope enrichment by SO_2-$NaHSO_3$ chemical exchange with closed reflux.



DICYCLOHEXYL 18-CROWN-6
$C_{20}H_{36}O_6$

FIGURE 9 - Configuration of the macrocyclic polyether dicyclohexyl 18-crown-6, $C_{20}H_{36}O_6$.