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DIRECT REDUCTION OF URANIUM HEXAFLUORIDE TO
URANIUM METAL BY USE OF SODIUM

by

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ABSTRACT

Thermodynamic considerations indicate that sodium should be favorable for the one-step reduction of UF_6 to uranium metal. A reaction vessel was developed for the continuous reduction of UF_6 to metal with batch collection of the products, and several experimental tests established the chemical feasibility of this direct and continuous reduction. Up to 93.5% of the uranium content of UF_6 continuously reduced by sodium in a reaction vessel was recovered as massive uranium metal in the form of a metal button of acceptable purity. A remaining problem is development of compatible materials of construction.

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1.0 INTRODUCTION

Much of the UF_6 product and tails from the gaseous diffusion process for isotopic separation of uranium as well as the UF_6 product from the Fused Salt-Fluoride Volatility process will ultimately be reduced to uranium metal.⁽¹⁾ So far, a two-step process with batch reduction has been adequate.^(2,3) However, a one-step, direct reduction of the UF_6 would be desirable, and a program was initiated to establish the chemical and engineering feasibility of such a process with reduction of UF_6 to metal by sodium.

2.0 PROCESS FLOWSHEET

A process flowsheet for sodium reduction of UF_6 should provide for both the primary reduction step and for a slag processing step for reclaiming uranium carried over in the NaF slag (Fig. 2.1). The slag processing step may not be necessary if low levels of uranium carryover are maintained.

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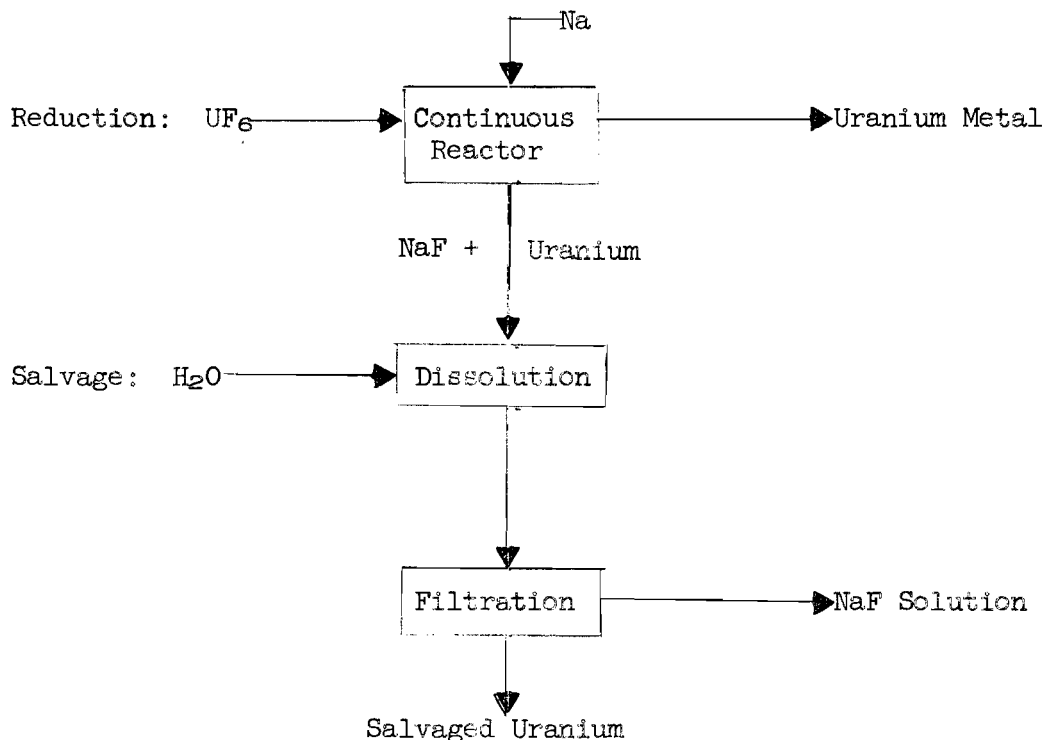


Fig. 2.1. Reduction and salvage process flowsheet.

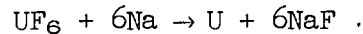
2.1 Reduction Step

In the reduction step, sodium and UF_6 in the gaseous form would be continuously reacted according to the stoichiometry

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The resulting slag (NaF) and uranium metal could be continuously removed from the reactor as liquids and separated by difference in specific gravity.

2.2 Slag Processing

If the slag contains dispersed uranium metal or incompletely reduced uranium compounds, the NaF could be dissolved in water and the solid uranium-bearing material filtered off and recycled. It is expected that the uranium-bearing solids will not be appreciably water-soluble.

3.0 THERMODYNAMIC CONSIDERATIONS

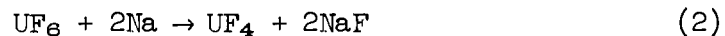
Standard free energy of reaction data indicate that any of the common alkali or alkaline earth metals are favorable for the reduction of UF_6 to uranium metal.⁽⁴⁻⁶⁾ Sodium was used in this work since it is cheaper and easier to handle from an engineering standpoint because of its low melting and boiling points, low slag (NaF) melting point, and high slag solubility in water.

3.1 Free Energy and Heat of Reaction

Thermodynamic calculations indicated that, over the temperature range of interest, the overall reaction



is favorable. The standard free energy change varies, over the temperature range 500-2000°K, from -276 to -96 kcal/g mole of UF_6 reacted (Fig. 3.1) and the standard heat of reaction from -313 to -82 kcal/g mole of UF_6 .⁽⁷⁾ The free energies of the reactions involved indicate that intermediate fluorides, particularly UF_4 , may also form at higher temperatures. The standard free energy change for the reaction



is always a large negative number, but that of



becomes positive at approximately 1875°K; therefore UF_4 may be a stable species at higher temperatures in this system.

3.2 Equilibrium Compositions

If the assumption is made that UF_4 , UF_3 , and U are the only uranium compounds present,⁽⁵⁾ the equilibrium composition of the UF_6 -Na reaction can be approximated. Since most of the thermodynamic data at the higher temperatures are extrapolated from much lower temperatures, and several component activities have to be approximated, the results of equilibrium calculations are qualitative. These calculations indicate equilibrium

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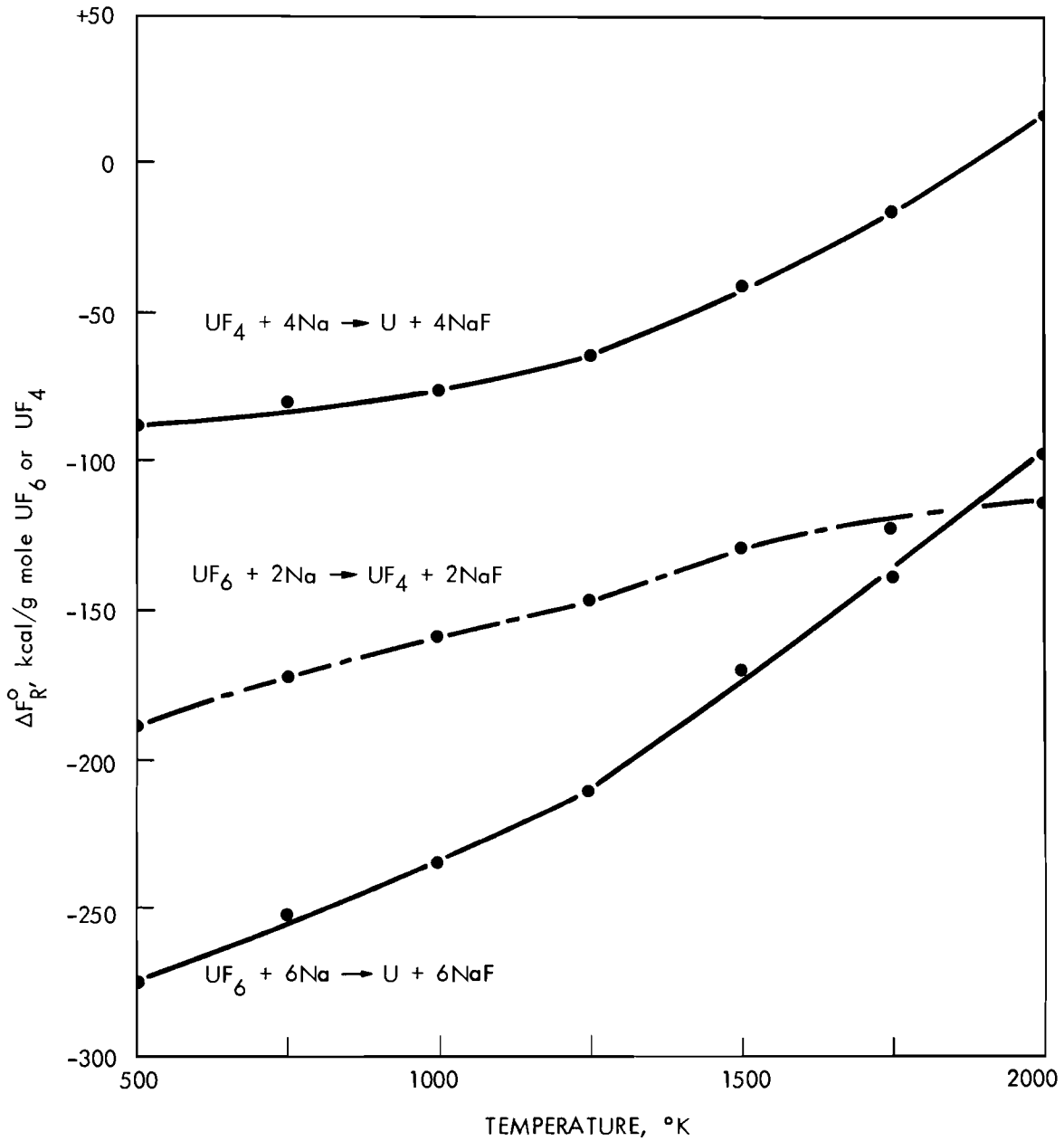


Fig. 3.1. Standard change in free energy for uranium reduction reactions with sodium. ΔF values from reference 7.

UF₄ and UF₃ contents of < 0.02% at the specific temperature of interest, 1200°C, although both species increase with increasing temperature.⁽⁵⁾ Thus, UF₆ should be essentially completely reduced to uranium metal if the kinetic mechanisms are sufficiently rapid. In the experimental program, no intermediate fluoride compounds were identified under conditions of excess sodium and good reactant mixing, although both UF₄ and a NaF-UF₃ complex were identified in trace amounts by x-ray analysis when there was a sodium deficiency.

3.3 Theoretical Reaction Temperature

The maximum theoretical reaction temperature for the UF₆ reduction with a stoichiometric amount of sodium was calculated to be 1704°K, the boiling point of NaF, when the reactants were initially at 100°C.⁽⁵⁾ This value indicates that the heat of reaction will probably be sufficient to maintain the reaction zone above the melting point of uranium metal, 1132°C.

4.0 EXPERIMENTAL PROGRAM

A semicontinuous reactor, for the continuous reaction of UF₆ with sodium and batch collection of the products, was developed. This development phase represented the major portion of the experimental effort.

4.1 Description of Assembled Reactor

The semicontinuous reduction reactor used in the latter part of the experimental program was a 6-in.-dia Inconel shell with top flange surrounding an insulated and graphite-lined reaction zone (Fig. 4.1). Holes through the top of insulating fire brick, MgO lid, and graphite lid were entrance ports to the reaction zone for a thermowell, the two reactant nozzles, and an off-gas line. The top flange of the reaction vessel allowed entry of the reactant nozzles, three thermowells, an inert gas purge line, and an off-gas line with 1/2-in. valve.

4.2 Reactant Entrance Nozzles

Since the system operated with excess sodium, there was a continuous sodium phase in the reactor in contact with the outlet of the UF₆ entrance nozzle. The UF₆-Na reaction appears to be very rapid, and reaction was significant at or near the tip of the UF₆ nozzle. This resulted in excessive temperature at the nozzle tip, which necessitated heat removal at that point to prevent melting or corrosion of the nozzle.

The most successful UF₆ nozzle design tested was one internally cooled with gas. It was a 1/8-in.-dia Inconel tube surrounded by an Inconel jacket, which allowed a cooling gas to circulate around the tube, thus removing heat from the hot portion (Fig. 4.2).

A 1/4-in.-o.d. stainless steel tube was used for the sodium inlet nozzle with no significant deterioration.

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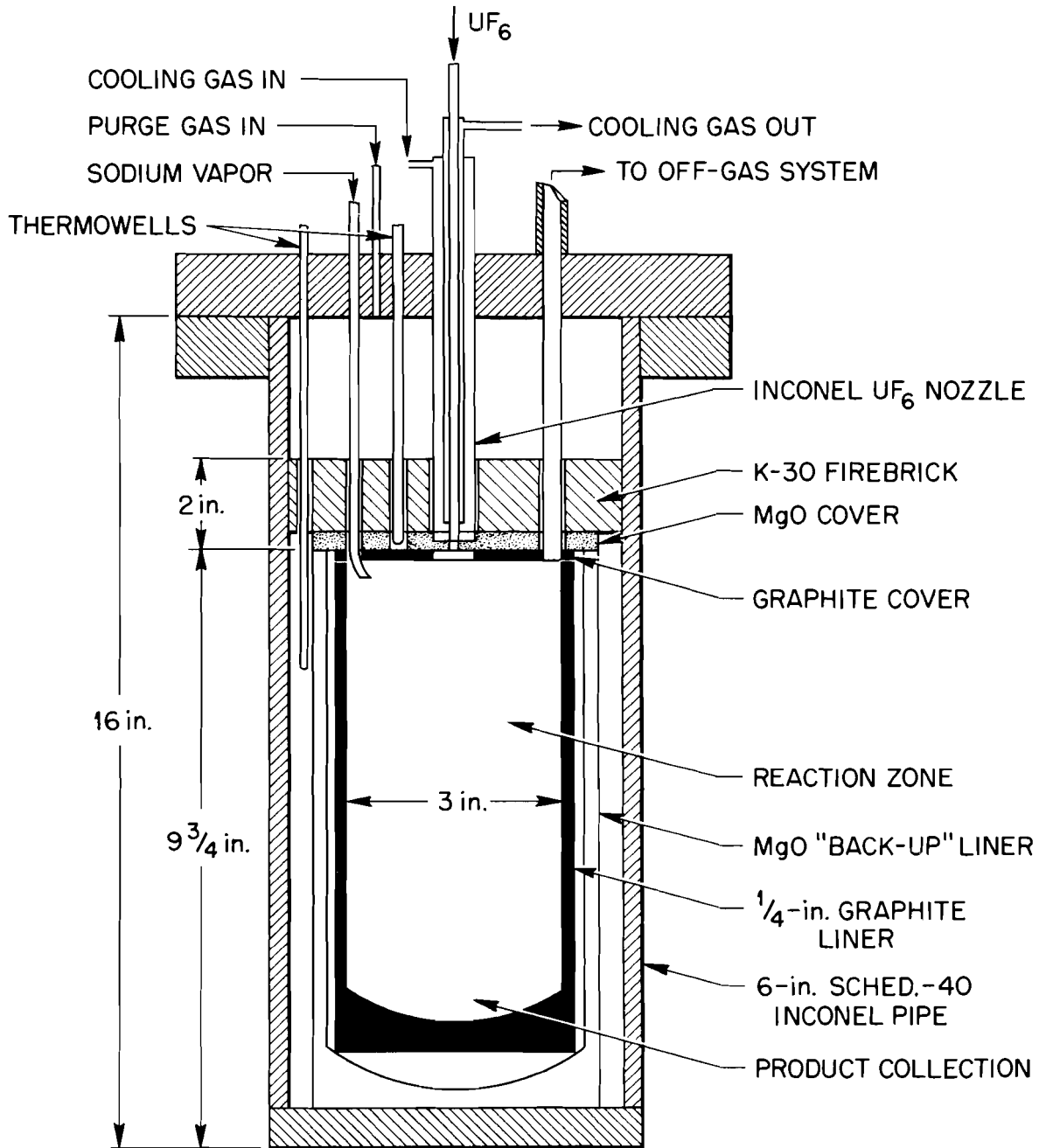


Fig. 4.1. Schematic of assembled reactor.

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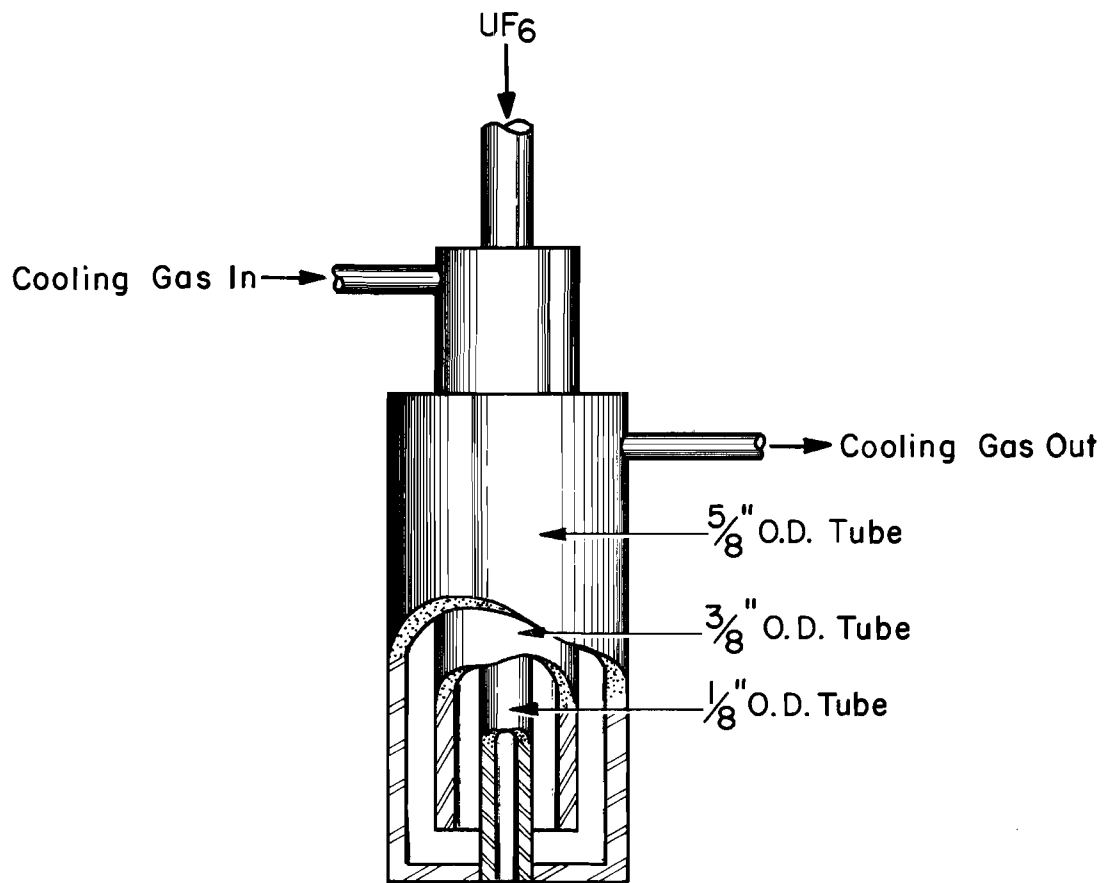


Fig. 4.2. Internally Cooled UF_6 Nozzle

4.3 Reaction Zone Containment

Reaction zone containment was another development problem. Although this phase of the development was not completed, a usable system was developed and possible revisions were indicated by experimental results.⁽⁹⁾ The containment zone design philosophy used was to completely contain the hot reaction zone and the resulting products while isolating them both physically and thermally from the reaction vessel proper. This isolation was necessary because of the high temperature and corrosive nature of the reaction zone environment and its incompatibility with the Inconel reactor.

Graphite withstood the temperature and corrosive action of the reaction zone better than either magnesium or alumina but cracked with severe thermal cycling, especially when sodium was present. The biggest problem with the graphite reaction zone liner was that the NaF slag wetted the graphite and escaped the liner because of the graphite porosity; however, graphite did contain the uranium metal formed. There is some evidence that a ceramic coating of low-porosity graphite may prevent escape of the NaF slag without decreasing the good thermal and corrosion resistance properties of the graphite. This type of graphite was not tested in the experimental program.

4.4 Auxiliary Equipment

The auxiliary equipment needed for the experimental facility (Fig. 4.3) consisted of (1) a sodium melting and metering section with provisions for vaporization prior to its entry to the reactor, (2) a UF_6 vaporizing and metering section, (3) an induction heater for initially heating the reactor to operating temperature, and (4) a reactor off-gas system capable of trapping sodium or UF_6 that escaped the reactor.

The sodium meter was an electromagnetic flow meter⁽⁸⁾ with control valve. UF_6 was metered by an instrumented orifice meter with constant pressure control. Reactor off-gas was treated by a cold trap for liquid sodium removal (packed column operating at $150^\circ C$) followed by an *n*-butyl alcohol wash to remove sodium vapor and calcium sulfate traps for UF_6 removal. All process lines were heated to above $100^\circ C$.

4.5 Experimental Procedures

For continuous reactor operation the reaction and product collection zones must be at temperatures above the melting point of uranium metal ($1132^\circ C$) to expedite separation of the NaF slag and uranium metal by difference in liquid specific gravities. A temperature of $1200^\circ C$ was chosen as the goal for operation of the reactor system.

In all experimental tests, the reaction zone was preheated to above the melting point of uranium metal ($> 1132^\circ C$). Sodium was then introduced to the reaction zone at a constant rate while helium was introduced through a UF_6 entrance nozzle to prevent plugging. Shortly after the initial sodium introduction, UF_6 was introduced at a constant rate that was less

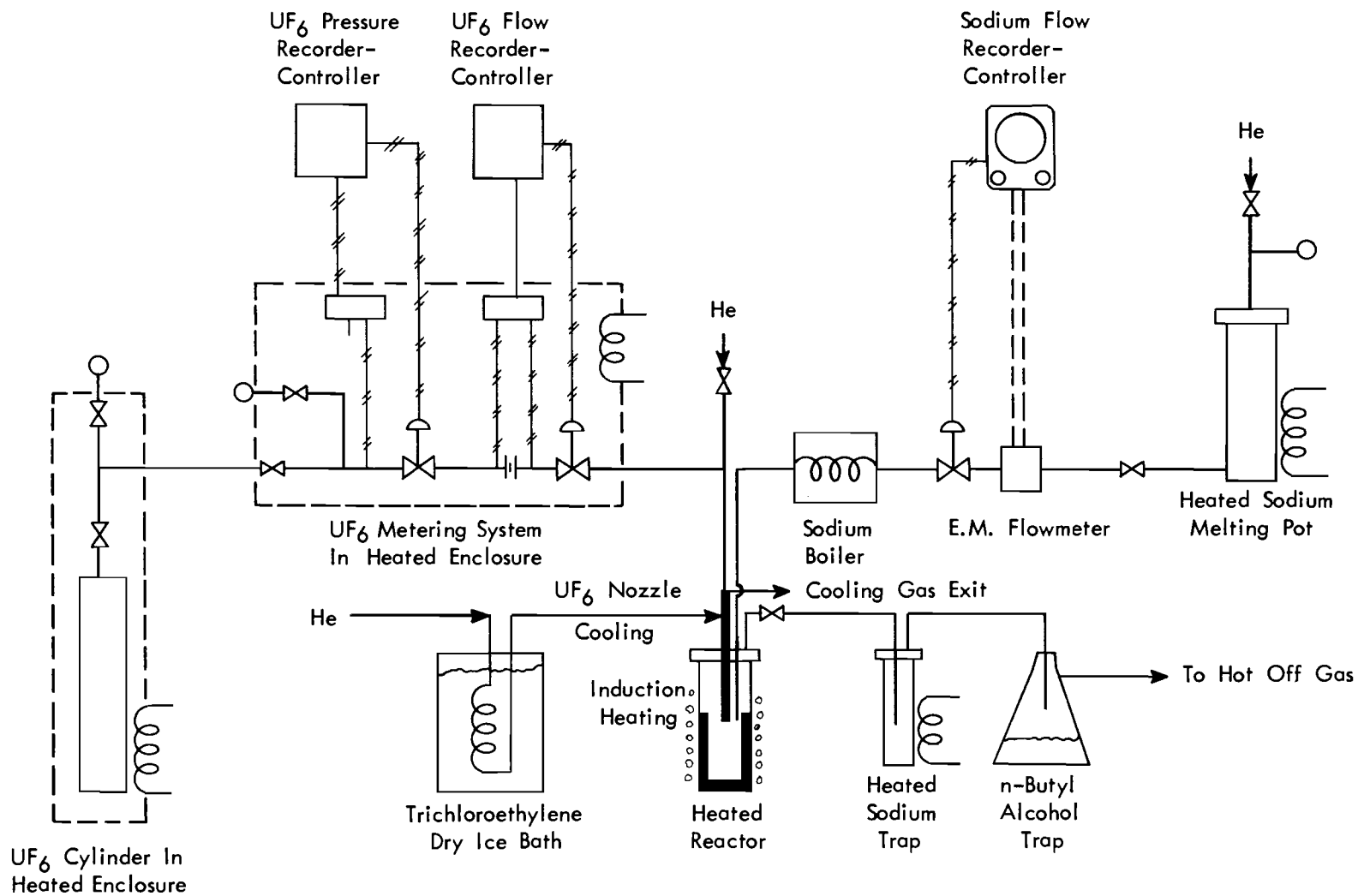


Fig. 4.3. Schematic of the experimental facility for study of the continuous reaction of UF_6 with sodium.

than the stoichiometric amount. The helium introduction rate to the UF_6 nozzle was gradually decreased until pure UF_6 was being introduced. The induction heating unit was turned off and the UF_6 and sodium rates were adjusted to give the proper reaction zone temperature from their heat of reaction. The run was allowed to progress until approximately a third of the reaction zone was filled with reaction products or there was an equipment malfunction.

5.0 EXPERIMENTAL RESULTS

A number of tests were made in the semicontinuous reactor, using various entrance nozzle and reaction zone containment designs.

5.1 Chemical Feasibility of Reduction

Although the main experimental program emphasis was testing the design of the various reactor components, some of the experimental results also indicated the chemical feasibility of the primary reduction equation, $UF_6 + 6Na \rightarrow U + 6NaF$. Several of the tests resulted in production and consolidation of significant quantities of uranium metal.

Although no test was entirely satisfactory from the standpoint of equipment serviceability, some conclusions may be made on the effect of operating variables on the reduction. In general, temperatures above the melting point of uranium were necessary for good metal consolidation and recovery. Sodium excess greater than 100%, but not exceeding 200%, appeared necessary for complete reduction, and relatively low UF_6 feed rates (< 40 g/min) were necessary to ensure good reactant mixing. These figures would be applicable only for the reactor geometry used in these tests.

In one run, 93.5% of the uranium introduced was recovered as consolidated uranium metal (any mass of metal with a dimension greater than 1/4 in.). This run ultimately was terminated because of off-gas line plugging. Both the graphite and MgO reaction zone liners in this test were removed intact, and the UF_6 nozzle was not damaged (Fig. 5.1).

5.2 Uranium Metal Purity

Uranium metal recovered from the more successful tests was consolidated in metal buttons found in the bottom of the graphite liner. These buttons were comparable in appearance to the metal buttons from small UF_4 -calcium bomb reductions (Fig. 5.2).

Although the UF_6 feed was not analyzed, complete chemical and spectrographic analyses of some of the metal buttons showed up to 99.9% uranium (Table 5.1), with the major contaminants, nickel and carbon, probably coming from the Inconel UF_6 nozzle and the graphite liner.

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Fig. 5.1. Intact crucible and liner after run in which 93.5% of the uranium was recovered as massive metal.

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Fig. 5.2. Uranium metal button from one reduction test.

Table 5.1. Analysis of Reduced Metal Product

Element	Amount	Element	Amount
U	99.9% ^a	Cu	8 ppm
C	0.036% ^a	Ga	< 0.5 ppm
Ni	0.019% ^a	Ge	< 0.5 ppm
Fe	0.014% ^a	Mg	41 ppm
Ag	< 0.2 ppm	Mn	1.3 ppm
Al	30 ppm		
B	< 0.5 ppm	Mo	< 1 ppm
Be	0.6 ppm	Pt	< 5 ppm
Ca	4 ppm	Ti	13 ppm
Cd	< 10 ppm	V	< 1 ppm
Cr	< 5 ppm	Zr	< 1 ppm

^a Chemical determination; others determined spectrographically.

5.3 Slag Recycle Feasibility

In order to test the feasibility of the proposed slag recycle scheme for recovering uranium-bearing material in the slag (Fig. 2.1), the amount of water-soluble uranium in the products of several runs was determined. The amount of uranium soluble in two hot water rinses of all reactor components was found to be less than 0.5% of the total uranium present in all products analyzed:

Uranium Material Balances in Three Experimental Tests, %

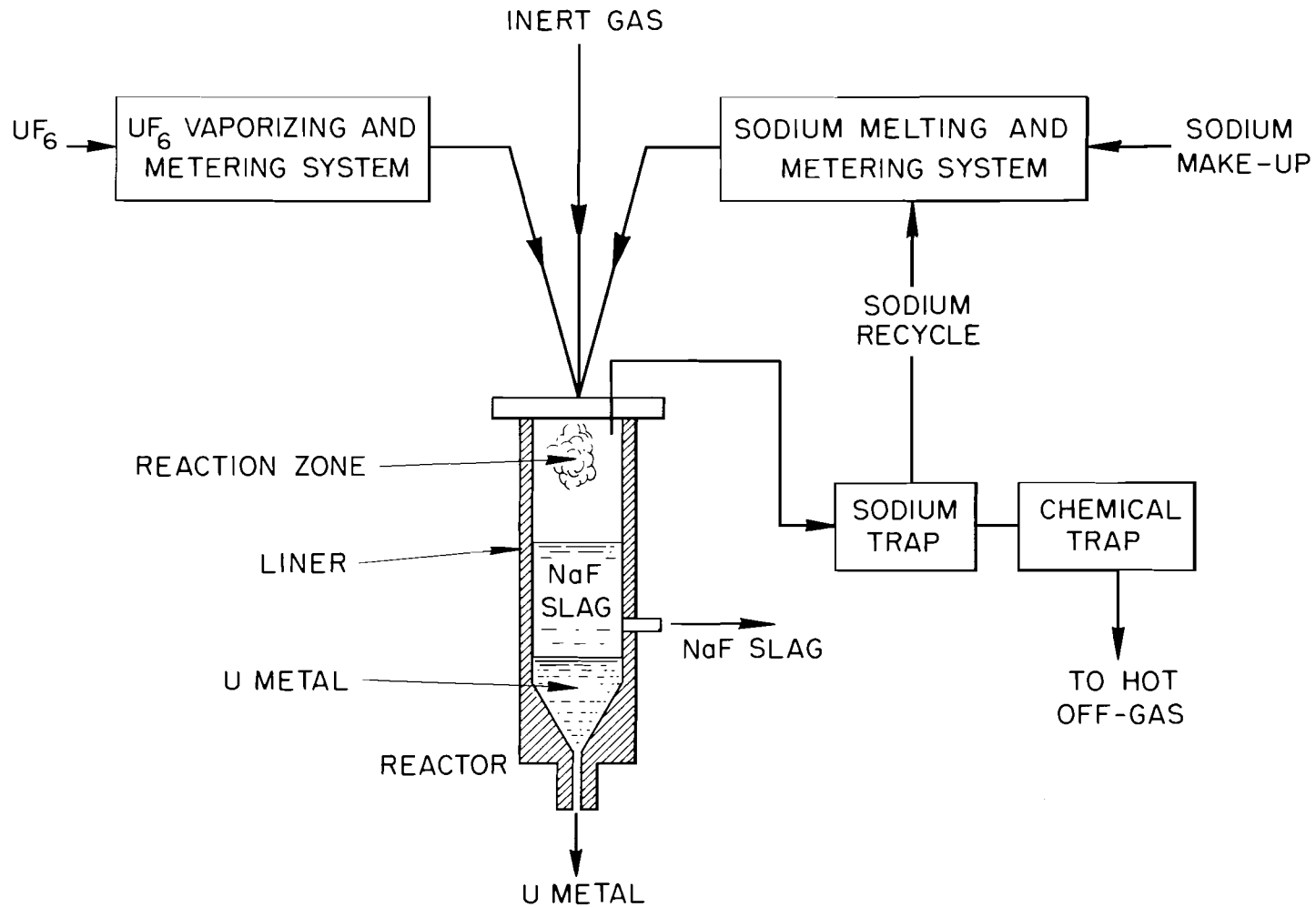
<u>Water-Soluble</u>	<u>As Massive Metal</u>	<u>In Other Solids</u>
0.40	19.7	79.9
0.03	41.7	58.3
0.30	82.3	17.4

If slag processing is necessary, water dissolution of the slag with recovery of the uranium-bearing material as a solid appears feasible.

6.0 EVALUATION AND APPLICATION OF REDUCTION PROCESS

The chemical feasibility of the direct reduction of UF_6 to metal by sodium was confirmed. The engineering feasibility of such a process has not been established, and additional engineering development will be necessary before complete economic evaluation of the process is possible.

A completely continuous reduction system would be desirable (Fig. 6.1), including provisions for metering UF_6 vapor and liquid sodium into a lined reaction vessel. The reactor would be at a temperature high enough to ensure that all products were liquid so that the metal could be readily



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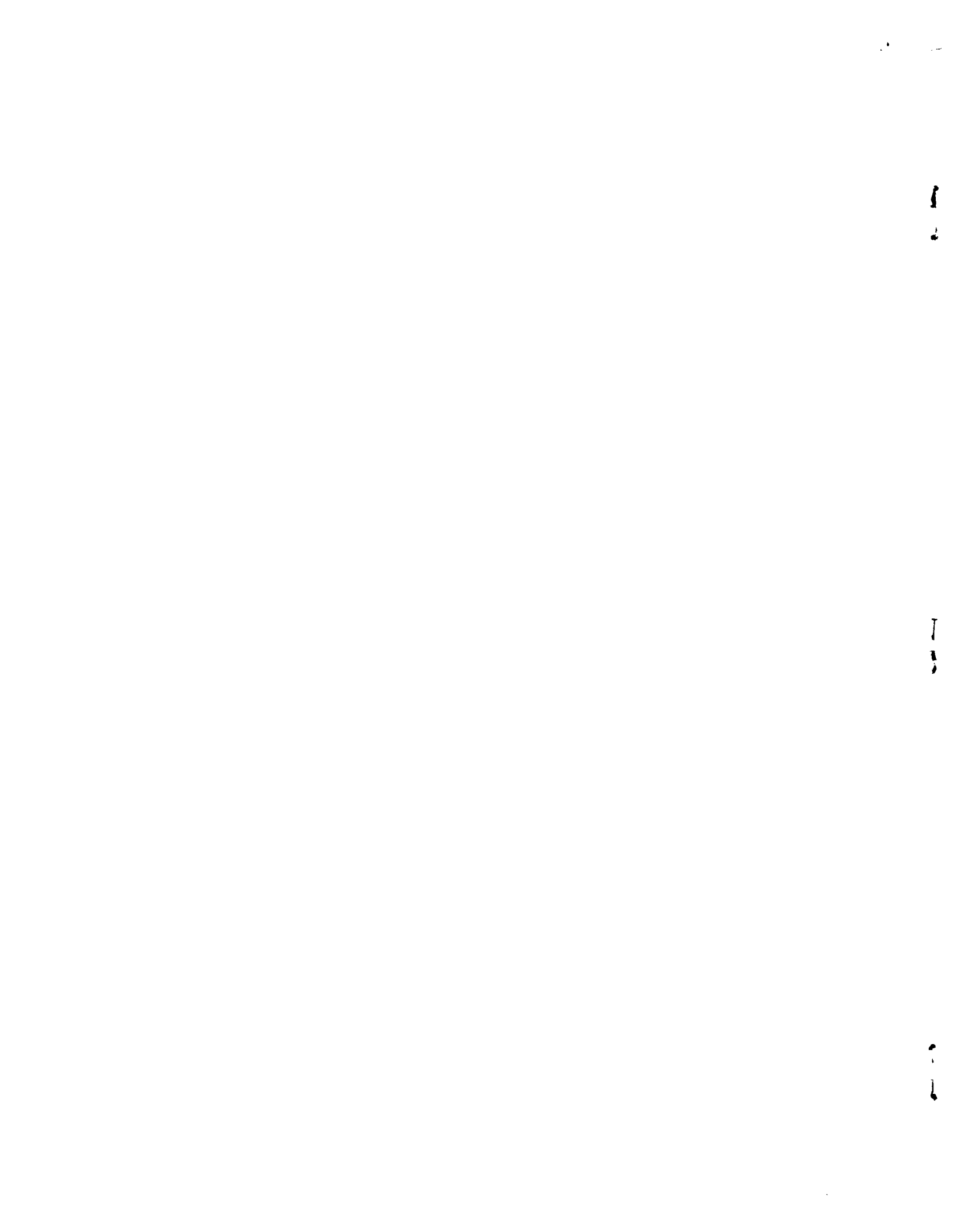
Fig. 6.1. Proposed continuous direct reduction of UF_6 to metal by use of sodium.

separated from the slag. There should be provisions for continuous removal of the products. An off-gas system would allow trapping and recycle of excess sodium.

Such a system, if operable, would offer several advantages over present methods, particularly for UF_6 highly enriched in U-235 in which nuclear criticality considerations are important. In such a system, small batch reductions are expensive, and use of the continuous reduction system with removal of uranium metal as a liquid may also by-pass the metal casting operation. It appears that the reactor size used in this development program could be operated critically safe with high U-235 enrichment by a combination of mass flow rate control and geometry control.

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