



AUSTRALIAN ATOMIC ENERGY COMMISSION
RESEARCH ESTABLISHMENT
LUCAS HEIGHTS

LABORATORY STUDIES OF AQUEOUS PROCESSES FOR THE
PRODUCTION OF HIGH PURITY URANIUM TETRAFLUORIDE
FROM AUSTRALIAN LEACH LIQUOR

by

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July 1976

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ABSTRACT

A modified form of the Power Reactor and Nuclear Fuel Development Corporation (PNC) process for the aqueous preparation of uranium tetrafluoride from Australian Rum Jungle leach liquor was investigated. The commercially available tertiary amine mixture, Alamine-336, was substituted for the more costly tri-n-octylamine in the amine purification section of the process; the extraction was examined by batch simulation of the countercurrent extraction, washing and stripping stages.

Alternative methods for reducing hexavalent uranium to the tetravalent state were examined and results on the use of powdered iron were encouraging. The use of hydrogen reduction appeared even more promising.

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1. INTRODUCTION

The majority of the uranium ores mined will be converted into uranium hexafluoride (UF_6), isotopically enriched in uranium-235, and fabricated into fuel elements for modern thermal nuclear power reactors. Historically, the manufacture of uranium hexafluoride from uranium ores has involved the production of a crude ore concentrate of uranium oxide (U_3O_8) at the mine sites, followed by transport to central refineries for purification of the uranium and its conversion into UF_6 . There are three major commercial processes for the manufacture of UF_6 ; all involve production of the intermediate, uranium tetrafluoride (UF_4).

The Power Reactor and Nuclear Fuel Development Corporation of Japan (PNC) has developed and reported a process by which pure UF_4 could be manufactured in mine site operations and which has been claimed to offer overall cost savings in the production of UF_6 [PNC, undated]. This report describes preliminary laboratory studies of the application of the PNC process to the preparation of UF_4 from sulphate leach liquors obtained from the Rum Jungle treatment plant and synthetic feed solutions prepared from yellowcake obtained from Rum Jungle. Several modifications to this process were investigated and a brief study of the influence of these changes on process economics was made.

2. SUMMARY OF AQUEOUS PROCESSES FOR MANUFACTURE OF URANIUM TETRAFLUORIDE

Table 1 summarises aqueous processes used in the manufacture of uranium tetrafluoride. In 1956, workers at Oak Ridge National Laboratory (ORNL) developed a method, known as the Excer process, for producing uranium tetrafluoride from aqueous solutions [Higgins & Roberts 1956; Marinsky 1956; Higgins, Neill & McNeese 1958]. In this process, ion-exchange resins were used to prepare purified, concentrated, aqueous solutions of uranyl chloride directly from sulphuric acid leach liquors, sulphate or chloride concentrates, or nitrate concentrates arising from solvent extraction processes. A chloride medium was preferred to sulphate because of the low decontamination factor for sulphur across the final precipitation stage. The uranium in solution was then reduced to the tetravalent state (U(IV)) either chemically, with metallic iron, or electrolytically and the uranium was precipitated by the addition of hydrofluoric acid to the heated solution. This 'green salt' ($UF_4 \cdot 3/4H_2O$) was collected and dried. The hydrated UF_4 was dehydrated on a stream of dry nitrogen by slowly raising the temperature to $400^\circ C$. Care was taken to avoid hydrolysis. The advantages claimed for the Excer process were its adaptability, reduction of the number of operations

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required, and the good decontamination achieved because there were two purification steps, viz the ion-exchange stage and the precipitation stage.

The Winlo process, developed in 1958 at the laboratories of the Winchester and National Lead Co. of Ohio [Allen, Petrow & Whitman 1958; Cselpo & Fogel 1964], substituted liquid ion exchangers for solid ion-exchange resins in the concentration and purification step, and a catalytic reduction stage was used to produce the U(IV) solution. The uranium in the leach liquor was extracted using a tertiary amine and stripped with hydrochloric acid to produce an aqueous solution of uranyl chloride. The uranium was then reduced in solution using sulphur dioxide gas with copper (II) as a catalyst. In the chloride medium, sulphur dioxide reduced the copper(II) to copper(I) ions which, in turn, reduced the uranium. The reduction was carried out at an elevated temperature in the presence of fluoride ions, and the tetrafluoride ($UF_4 \cdot 3/4H_2O$) was precipitated as uranium was reduced. The $UF_4 \cdot 3/4H_2O$ was air dried at $110^\circ C$ to remove all moisture except water of hydration. The sample was then placed in Monel trays and heated quickly to a temperature of $500^\circ C$ in a Monel tube furnace, vented to the atmosphere at both ends, for forty minutes. The oven was quickly cooled while flushing with air. The originators of the process claimed a more dense product than that obtained from the Excer process.

Investigators at Dow Chemical Company, Pittsburg, California, reported a variety of methods for obtaining high purity uranium tetrafluoride from aqueous solutions [Long, Ellis & Magner 1958]. They employed alkyl phosphates, amines or ion-exchange resins for uranium recovery from the sulphate leach liquor. The uranium in the stripped solution was reduced chemically (with iron) or electrolytically, and the tetravalent uranium was further purified with an amine or alkylphosphate before precipitation of a hydrated tetrafluoride of unstated composition.

The French process for double fluoride preparation [Brodsky & Pagny 1958] was developed further in South Africa [Robinson, Geertsma & Paynter 1964] for UF_4 production. The $UF_4 \cdot NH_4F$ was precipitated by sulphur dioxide from a solution containing ammonium fluoride, uranyl nitrate, and formic acid at about $80^\circ C$. Uranous ions, formed by reduction of hexavalent uranium with nascent hyposulphurous acid, combined with the alkali fluoride to precipitate the unhydrated uranous ammonium salt, which was decomposed to UF_4 by heating in a fluidised bed.

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The SIMO process, developed in France by the Société Industrielle de Minerais de l'Ouest and installed at the Eurochemic reprocessing plant at Mol, Belgium, used purified uranyl nitrate as feed material [Weinhold 1970]. Conversion to the sulphate form was achieved by heating the uranyl nitrate with concentrated sulphuric acid at approximately 120°C; this was followed by electrolytic reduction at 50°C and precipitation of $UF_4 \cdot 3/4H_2O$ at 95°C.

The Power Reactor and Nuclear Fuel Development Corporation of Japan recently announced the development of the PNC process [Takada, Amanuma & Fukuda 1971]. This process combined features from both the Excer and Winlo processes. Uranium was recovered from the sulphate leach liquor by extraction with the tertiary amine, tri-n-octylamine (TNOA). While still in the organic phase, the uranium was converted from a sulphate to a chloride species by washing with 8 M HCl. The chloride species was then stripped from the organic phase with 0.05 M HCl, electrolytically reduced, and then hydrofluoric acid was added to precipitate uranium as the hydrated tetrafluoride at 95°C. The UF_4 hydrate was dehydrated at 350°C under nitrogen gas. The amine solvent and the chloride were recycled. Figure 1 compares the PNC process with the Excer process and other processes used in commercial conversion plants.

The PNC process was tested on a pilot plant at the Ningyo-toge mine in Japan, using uranium ores containing 0.03-0.15% U_3O_8 . The product was claimed to be of reactor grade (nuclear purity) and the production cost lower than that of the conventional process.

3. EXPERIMENTAL

3.1 Materials and Reagents

All chemicals used in these studies were of reagent grade or the highest purity obtainable from commercial sources, with the exception of those described below.

Initially, two uranium feed solutions were prepared from Rum Jungle yellowcake (Table 2), simulating only the uranium, sulphate and acid concentrations of a pregnant liquor used at the Ningyo-toge pilot mill (Feed A) and a typical Rum Jungle leach liquor (Feed B). These feed solutions were obtained from a concentrated stock solution by suitable dilution and adjustment of sulphate and pH. The stock solution was prepared by the dissolution of Rum Jungle yellowcake in a minimum quantity of 5 N HNO_3 at 96°C, ageing for one hour at room temperature, filtering to remove suspended iron and silica, adding concentrated sulphuric acid and heating to a temperature of 120°C for a minimum of one hour to remove the

nitrate, adjusting the sulphate content to 2.0 M after sulphate analysis [Archer 1957] and diluting to volume. The third uranium feed solution (Feed C) was aged sulphate leach liquor procured from the Rum Jungle treatment plant. Since the available volume of this latter solution was small, all preliminary investigations were made with Feeds A and B and the final evaluation of the process was tested on Feed C.

3.2 Equilibration Technique

Extraction coefficients (E_a^0), defined as the ratio of the concentrations in the organic and aqueous phases, were determined by shaking the appropriate volumes of the two phases in suitably sized separating funnels at room temperature (*i.e.* $\sim 20^\circ\text{C}$), separating the two phases, and then determining the uranium by the method of Florence [1971].

For convenience in these laboratory studies, the extraction, conversion and stripping tests of the solvent extraction purification cycle used in the PNC process (Figure 2) were performed by batch simulation of counter-current extraction as suggested by Haas [1961]. Figure 3 summarises the equilibrations and the appropriate flow of the phases in the simulation of the extraction cycle. Equilibrations were performed in separating funnels at room temperature for five minutes. The solutions were allowed to stand for five minutes before the phases were separated. If the phases failed to separate in this period, the conditions were noted and the phases were separated by centrifuge. The phase ratios and volumes used in each series of equilibrations are listed in Table 3.

3.3 Electrolytic and Chemical Reduction

Electrolytic reductions were performed in a jacketed cell employing a mercury cathode and a platinum foil anode enclosed in a glass tube containing 1.0 M H_2SO_4 and sealed with a sintered glass plug. A current of 0.4 A was used for a 10 cm^3 aliquot of solution, 1.5 N in HCl. The cell was maintained at room temperature and the reduction continued until the first sign of brown U(III) appeared in the solution. Air was then bubbled through the solution to oxidise the U(III) to the dark green U(IV). The extent of the reduction was determined by polarographic assay of U(VI).

Metallic iron, magnesium, aluminium and zinc were also examined as reductants for the reduction of U(VI) to U(IV). The determination of U(VI) by polarography was used to follow the reduction. Initially, the potential between an inert platinum and a saturated calomel electrode was continuously recorded throughout the reduction using an EIL Model 23A pH meter as a millivoltmeter. This method was replaced later by the

technique of differential electrolytic potentiometry; in this technique, a constant current is imposed across two platinum electrodes and the potential measured as the U(VI)/U(IV) ratio changes [Bishop & Dhaneshwer 1964]. A factor affecting the suitability of a chemical reductant was its decontamination in the subsequent uranium tetrafluoride precipitation stage.

3.4 Uranium Tetrafluoride Precipitation

All precipitation studies were performed in a Teflon tube immersed in a heated oil-bath (Figure 4). When the reduced uranium solution reached 96°C, a 10 per cent stoichiometric excess of 40 per cent hydrofluoric acid was slowly added while the solution was stirred with a magnetic stirrer. A polythene air condenser was fitted to the Teflon tube and the solution agitated for a further hour. The solution in the Teflon tube was centrifuged and the supernatant withdrawn. The tube was replaced in the oil-bath and more hydrofluoric acid was added, amounting to 10 per cent of the original quantity, together with boiling demineralised water, equal in volume to the supernatant withdrawn. The solution was stirred for several minutes and then centrifuged again. After removal of the supernatant, the tube was replaced in the heated oil-bath and left for an hour. This eliminated all moisture except the water of hydration. The supernatant was then analysed for uranium.

An alternative washing procedure to that described above was also studied. The UF_4 hydrate was filtered through a 05 grade Poral monel filter disc (Ugine-Carbone, Alan H. Reid, Sydney) set in an all-Teflon filter apparatus as shown in Figure 5. With the suction off, a hot (~90°C) dilute solution of hydrofluoric acid (10-15 cm³) was added and stirred for several minutes with a magnetic stirrer before filtering with suction. The washing was repeated and the product dried at 100°C in an air oven.

4. RESULTS AND DISCUSSION

4.1 Uranium Purification by Amine Extraction

The chloride conversion process of the PNC flowsheet was tested on the two synthetic feed solutions A and B (Table 2) before extending the process to Feed C (Rum Jungle leach liquor). For these experiments, 0.2 M tri-n-octylamine (TNOA) in odourless mineral spirits (OMS) modified with 6 vol.% 2-ethylhexanol was used in the extraction cycle, 8 M HCl in the wash cycle and 0.05 M HCl for stripping the uranium. At the conclusion of these extraction studies, the purification cycle was repeated as described above after substituting the commercially available tertiary amine mixture (Alamine-336) for TNOA, while the solvent (OMS modified with 6 vol.%

2-ethylhexanol) remained unchanged.

4.1.1 Amine extraction

Preliminary investigations with both tertiary amines (TNOA and Alamine-336) on a synthetic uranium feed revealed little difference in the extent or kinetics of their extraction of uranium (Table 4).

Using the same synthetic feed prepared from yellowcake, the extraction with both amines proceeded smoothly with rapid separations of the phases. However, the Rum Jungle leach liquor (pH 1.35) formed stable emulsions at each extraction stage. Standing for twelve hours had little effect on these emulsions nor did a change in the concentration of modifier. Therefore, the phases were separated by centrifuging before analysing for uranium.

The emulsion properties of both solvents in batch equilibration tests were compared with those of an amine purification process using filtered Rum Jungle leach liquor in a laboratory mixer-settler plant developed by Ryan [1973]. An organic solvent, 0.1 M Alamine-336 in OMS modified with 3 vol.% nonanol, formed no emulsion in these mixer-settlers. However, when adapted to AAEC batch equilibration tests, this solvent also formed emulsions, thereby suggesting that the violent agitation in the laboratory batch tests was causing emulsion formation.

Table 5 summarises the results of uranium analysis in each extraction, washing and stripping cycle as well as those for the PNC process [Takada, Amanuma & Fukuda 1971]. Using TNOA as the extractant with Feed A (column 1) yielded very similar results in the extraction cycle to those published for the PNC process (column 5). The results for Alamine-336 (column 3) were slightly inferior, but the higher sulphate content and lower acidity of the Rum Jungle leach liquor (Feed C) aided the higher uranium loading in the organic phase for both solvents (columns 2 and 4).

Comparison of the extraction properties of the two amines reveals that TNOA is superior in the low sulphate (0.24 M), high acidity (pH 1.1) solution, whereas Alamine-336 is only marginally superior in the high sulphate (0.38 M), low acidity (pH 1.35) solution.

Table 6 compares the uranium concentration in the organic phase at various stages during the extraction cycle for the Alamine-336 extractant and Rum Jungle leach liquor feed with that of the PNC process [Takada, Amanuma & Fukuda 1971]. The marked difference in the loading rates reflects the differences between the initial uranium concentrations in the two feeds. The similarity between the figures in the final stage indicated that the solvent had reached maximum loading.

4.1.2 Chloride conversion cycle

The washing cycle, which involves contacting the loaded organic phase with 8 M HCl, converts the uranium from a sulphate to a chloride complex form. During this cycle a third phase formed, predominantly at the bottom of the organic phase. The results were the same for both extractants although occasionally, with the synthetic feeds, no such effect was noted. Further additions of 2-ethylhexanol or substitution of octanol in the organic phase failed to eliminate third phase formation. The volume of the aqueous wash phase decreased by less than 5 per cent, showing that entrainment losses were not large. The third phase persisted through both stages of the washing cycle, but was eliminated in the first stage of the stripping cycle. Generally, the uranium losses to the aqueous wash phase or conversion liquor were lower than that for the PNC process (Table 5).

4.1.3 Aqueous stripping cycle

No difficulties were encountered during the stripping cycle with 0.05 M HCl. Phase separations were rapid and the uranium loadings in the aqueous phase were as good as, and sometimes superior to those recorded in the PNC process. Both amines performed equally well with Rum Jungle leach liquor.

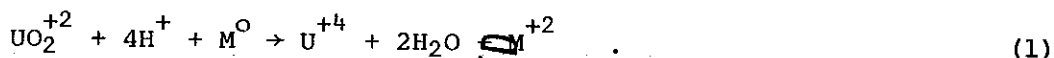
4.2 Uranium Reduction

4.2.1 Electrolytic reduction

Electrolytic reductions proceeded with no apparent problems, colour changes in the solution being used to determine the completion of the reduction. The time taken for the reduction was about 45 minutes. Except for one test, the concentrated and purified strip product ($\geq 100 \text{ g U l}^{-1}$) from the Amex chloride conversion process was used as feed for the reduction cell. In the excepted case, the Rum Jungle leach liquor, without prior treatment, was fed to the cell and the current passed for 15 minutes. During the reduction, a pink-mauve solution formed around the platinum foil inside the glass sheath. It was thought that this was due to the presence of manganese, and qualitative chemical tests supported this view.

4.2.2 Chemical reduction

The metals aluminium, magnesium, zinc and iron were examined as possible reductants for the reduction of U(VI) to U(IV). The reactions of interest are:



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Reaction (2) must be minimised otherwise a large excess of reductant is necessary for complete reduction of the uranium.

Both aluminium and magnesium were discarded after initial studies because of their extreme reactivity in dilute acid solution and their ready consumption by reaction (2). Investigations also showed that zinc participated primarily in reaction (2) when impure uranium feed solutions were used. However, since the reduction step follows the amine purification cycle and chloride conversion step, the uranium is normally in a relatively pure solution. Using high purity uranyl chloride solutions prepared from laboratory reagents, only 15-20 per cent excess zinc above the stoichiometric quantity was needed for the reduction.

All studies were performed on 0.4 M uranyl chloride solutions approximating the concentration of the feed to the PNC reduction plant. The theoretical amount of acid used in the reduction reaction is 1.6 M, so the electrochemical reduction was investigated in various uranyl chloride solutions of fixed uranium concentration but whose acidities were adjusted to 1.0 M, 1.6 M, 2.0 M and 3.0 M, respectively, with hydrochloric acid. These showed that neither the reduction rate nor the degree of reduction varied significantly over this range of acidity (Figures 6 and 7). For metallic iron, 10 per cent excess was needed for more than 95 per cent reduction of U(VI). Zinc was less efficient as a reductant owing to its partial involvement in reaction (2). Using either of the reductants with the 1 M acidity solutions led to the formation of a thick clear gel on ageing caused, no doubt, by the production of U(IV) in an acid deficient system.

Potentiometric measurements were carried out as a function of added metal, using platinum and saturated calomel electrodes; however, these were erratic and failed to indicate when the reduction was complete. This arose from the sluggish manner in which equilibrium potentials for the U(VI)/U(IV) couple were established. However, the technique of differential electrolytic potentiometry developed by Bishop & Dhaneshwar [1964] proved successful in the detection of the end point. Figure 8 summarises the resulting curves for both zinc and iron.

Choice of a metallic reductant is also dependent on the effective decontamination of these added impurities from uranium during the precipitation of uranium tetrafluoride. Investigation showed that the degree of

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decontamination was a function of the washing of the hydrated UF_4 precipitate. Decontamination was poor when decantation was used but increased substantially with filtration and repeated washing of the precipitate on the filter. The corrosive nature of the precipitation medium restricted the choice of filters. Good results were obtained with a Monel filter disc. With iron as reductant, the iron content in the dried UF_4 product was $55 \mu\text{g g}^{-1}$; when zinc was substituted, the residual zinc concentration was $125 \mu\text{g g}^{-1}$.

4.2.3 Comparative economics for the production of reduced uranium

Table 7 summarises a preliminary comparison of the costs of electrolytic reduction and various chemical methods. Costing is in 1975 Australian monetary units. The electrolytic reduction stage of the PNC plant with a capacity of 4.2 Mg U per day was quoted by PNC [undated] as costing $\$2.32 \times 10^6$, excluding site preparation, laboratory, shipping and warehouse facilities. The energy consumption was listed as $1.84 \text{ kWh kg}^{-1} \text{ U}$. It was assumed that the plant operated on a 3-shift, 24-hour basis for 250 days per year. The plant was amortised over 5 years at an interest rate of 10 per cent with no residual value, the debt/equity ratio was 50 per cent, the return to equity was 15 per cent (after tax) and taxation was 47.5 per cent on equity. Capital costs included an allowance for pre-operational charges of 10 per cent interest on 50 per cent of the capital for one year. It was estimated that the additional amount of labour required by the electrolytic reduction method, compared with any of the chemical reduction methods, is 2 operators per shift at $\$10,000$ per man including overheads. The comparative cost for the electrolytic reduction stage at the mine site is $90 \text{ ¢ kg}^{-1} \text{ U}$.

Australian capital costs are significantly lower in the chemical reduction plants using iron and zinc powders, and are estimated at $\$A250,000$ on the same basis of the electrolytic reduction plant. In particular, a rotary drum vacuum filter is assumed instead of the simple decanter used with the electrolytic plant for separation and washing of the UF_4 hydrate, to avoid contamination of the product. Energy costs are negligible for the chemical reduction processes, but additional sulphuric acid in the hydrochloric acid recovery plant, additional wash water for filtration, and chemicals for waste treatment by neutralisation are required at estimated costs of 6.9 and $8.8 \text{ ¢ kg}^{-1} \text{ U}$ for the iron and zinc reduction processes, respectively.

Consideration has also been given to the use of hydrogen as a reductant. Theoretically, 8 g is required for the reduction of each kilogram of uranium

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but, for practical applications, it is assumed that a 20 per cent excess is necessary. The price of hydrogen was taken as 21.2 ¢ kg⁻¹ (recalculated from Charlesworth & Schmidt [1965]). Capital charges for hydrogen reduction are considerably less than metal reduction since decanters can be used after the precipitation stage as for electrolytic reduction. There are no additional waste and acid recovery processing costs with hydrogen reduction. While platinum catalyst is required in this reduction reaction, it can be continuously recycled. Work on the Sol-Gel process at ORNL showed that 30 g of platinum catalyst is required to reduce 0.88 kg⁻¹ U per hour [Wymer 1968]. Continuous recycle would place a capital charge of 0.8 ¢ kg⁻¹ U on this item, while three complete changes of catalyst in five years would cost 2.5 ¢ kg⁻¹ U and three changes per year would cost 9.2 ¢ kg⁻¹ U.

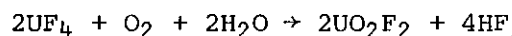
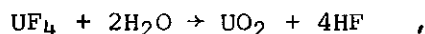
The estimated comparative costs for the various reduction processes show that chemical reduction appears significantly cheaper than electrolytic reduction. In particular, catalysed hydrogen reduction appears attractive because it costs the least and does not introduce the possibility of contamination of the product (as in the case of iron and zinc); clearly, it warrants further investigation.

4.3 Uranium Tetrafluoride Precipitation

Precipitation of the tetrafluoride at temperatures exceeding 90°C by the addition of a 10 per cent excess of 40 per cent hydrofluoric acid ensures the formation of the crystalline product UF₄.3/4H₂O. At lower temperatures, the gelatinous fluoride UF₄.5/2H₂O forms; it is difficult to handle, more susceptible to contamination and yields a low density product. Therefore, centrifuging and washing of the precipitate were performed at elevated temperatures (95°C).

Generally, the uranium recovery from the reduction and precipitation steps exceeded 90 per cent, as determined by weighing the dried precipitate and by uranium analysis of the supernatant. However, when a dilute uranium solution was used (untreated Rum Jungle leach liquor), the uranium recovery was as low as 68 per cent. Thus, the precipitation of tetrafluoride from dilute leach liquor is impractical.

The dehydration of the tetrafluoride hydrate was not examined in these laboratory studies but the literature warns that the process can be complicated by two side reactions:



Most workers heated the $UF_4 \cdot 3/4H_2O$ to 400-500°C under a nitrogen blanket (see Section 1).

4.4 Purity of the Uranium

Samples of the feed and strip solutions from the amine extraction section and the uranium tetrafluoride products were submitted for general spectrographic analysis for fifteen elements. The results of these analyses (Table 8) show that the majority of the decontamination occurred in the amine extraction section of the process.

Table 9 compares the purity of the UF_4 product derived from the Rum Jungle leach liquor using TNOA with the published figures obtained by the PNC process at Ningyo-toge mine site. The figures reveal that the uranium tetrafluoride purity is slightly inferior to the nuclear grade PNC product but compares favourably with the specification listed for Canadian UO_2 . Substitution of Alamine-336 for TNOA yielded similar concentrations of impurities in the UF_4 .

4.5 Alternative Scheme

An alternative reduction/purification scheme was examined involving chemical reduction of the uranium with metallic iron and then purification of the tetravalent uranium. However, the results were not encouraging owing to the difficulties in maintaining uranium in the tetravalent form, its participation in hydrolytic reactions and the low selectivity of U(IV) solvent extraction chemistry.

Elimination of the amine purification and concentration cycle yielded low amounts of impure UF_4 . The electrolytic stage proceeded with very low current efficiencies, and the decontamination across the precipitation stage using a dilute U(IV) feed was insufficient to yield a pure product.

5. CONCLUSIONS

The commercially available tertiary amine mixture (Alamine-336) is recommended as a substitute for tri-n-octylamine (TNOA) in the amine purification section of the PNC process. Although some emulsion problems were encountered in a batch simulation of the extraction process using a Rum Jungle leach liquor ($1.0 \text{ g U } \ell^{-1}$, 0.38 M sulphate, pH 1.35), the trouble was attributed to the laboratory equipment rather than to the physical or chemical properties of the phases.

Laboratory studies showed that the capital and energy-intensive electrochemical reduction process for reducing U(VI) to U(IV) can be replaced by a more economical chemical reduction step using finely powdered iron without exceeding the iron concentration listed by PNC for their final UF_4

product.

The use of hydrogen for the reduction of uranium promises further economic advantages over metallic iron.

The purity of the UF_4 obtained from aged Rum Jungle leach liquor compares favourably with published data for PNC-derived UF_4 .

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TABLE 1

AQUEOUS PROCESSES FOR THE PRODUCTION OF HIGH PURITY UF₄

Process	Country of Development	Date	Outline
Excer	USA	1956	(a) Ion exchange; chloride conversion; water strip; chemical or electrolytic reduction; precipitation. (b) Later version: anion exchange; sulphate elution; iron reduction; anion exchange; sulphate elution; cation exchange; chloride elution; precipitation.
Winlo	USA	1958	Amine extraction; chloride conversion; reduction-precipitation with SO ₂ /copper/HF.
Dow	USA	1958	Ion exchange; amine or phosphate extraction; iron or electrolytic reduction; second stage solvent extraction; precipitation.
'French'	France South Africa	1958 1964	Ammonium uranium fluoride precipitation with SO ₂ and fluoride.
SIMO	France	1970	Uranyl nitrate feed; sulphate conversion; electrolytic reduction; precipitation.
PNC	Japan	1970	Amine extraction; chloride conversion; electrolytic reduction; precipitation.

TABLE 2

COMPOSITION OF URANIUM FEED SOLUTION, A

	Feed A	Feed B
U concn. (g l ⁻¹)	0.42	1.00
Total sulphate, (M)	0.24	0.38
pH	1.10	1.35

TABLE 3

CONDITIONS FOR BATCH SIMULATION
OF PNC-SOLVENT EXTRACTION PROCESS

	Feed A	Feed B
<u>Extraction Cycle</u>		
A_o/E_o	20.8	8.8
A_o (cm ³)	1000	500
E_o (cm ³)	48	56.8
<u>Wash Cycle</u>		
E_o/W_o	5.5	5.6
E_o (cm ³)	47.5	56.0
W_o (cm ³)	8.6	10.0
<u>Strip Cycle</u>		
E_o/S_o	10.5	10.5
S_o (cm ³)	2.0	2.28
E_o (cm ³)	21.1	24.0

A_o : Table 2; E_o : 0.2 M Amine in OMS
+ 6 vol.% 2-ethylhexanol
 W_o : 8 M HCl; S_o : 0.05 M HCl

TABLE 4

EXTRACTION OF URANIUM(VI) BY 0.2 M AMINE
AS A FUNCTION OF TIME

Amine	Extraction Coefficients		
	1 min	5 min	60 min
Alamine-336	44.9	61.5	104.8
TNOA	47.8	56.5	109.1

Organic diluent: OMS + 6 vol.% 2-ethylhexanol
Aqueous phase: 0.42 g U l⁻¹; 0.24 M SO₄;
pH 1.1 (Feed A)

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TABLE 5
URANIUM CONCENTRATION PROFILE IN BATCH EXTRACTION TRIALS

Feed	A	C	A	C	Takada et al. [1971]
Uranium	Rum Jungle Yellowcake	Rum Jungle Leach Liquor	Rum Jungle Yellowcake	Rum Jungle Leach Liquor	Ningo-toge mine
Amine	TNOA	TNOA	336	336	TNOA
U concn. - feed ($g\ l^{-1}$)	0.42	1.0	0.42	1.0	0.44
Sulphate concn. (M)	0.24	0.38	0.24	0.38	0.24
Feed pH	1.10	1.35	1.10	1.35	1.10
U concn. - loaded organic ($g\ l^{-1}$)	9.30	9.82	8.75	10.07	9.33
U concn. - raffinate ($g\ l^{-1}$)	0.002	0.012	0.012	0.037	0.001
U concn. - aq. conv. liquor ($g\ l^{-1}$)	0.064	0.135	0.108	0.103	0.110
U concn. - stripped organic ($g\ l^{-1}$)	0.036	0.092	0.002	0.084	0.027
U concn. - aq. strip. ($g\ l^{-1}$)	150	129	108	128	106

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TABLE 6

URANIUM CONCENTRATION PER STAGE OF EXTRACTION CYCLE IN THE
PNC-SOLVENT EXTRACTION PROCESS

Amine	Feed	Uranium Concentration (g l ⁻¹)				References
		First Stage	Second Stage	Third Stage	Fourth Stage	
TNOA	PNC	0.073	0.135	1.25	9.33	Takada et al. [1971]
Alamine-336	Rum Jungle leach liquor	0.876	10.180	9.95	10.15	This work

TABLE 7

APPROXIMATE COMPARATIVE COSTS FOR VARIOUS REDUCTION PROCESSES, JAN., 1975

Reduction Processes	Electrolytic	Iron	Zinc	Hydrogen
Capital investment	\$2,320,000	\$250,000	\$250,000	\$100,000
Power consumption (kWh kg ⁻¹ U)	1.84	0.002	0.002	0.001
Unit material cost (¢ kg ⁻¹ U)	-	21.3	53.5	21.2
Material usage (kg kg ⁻¹ U)	-	0.25	0.31	0.01
Material cost (¢ kg ⁻¹ U)	-	5.4	16.6	0.2
Capital cost	80.6	9.2	9.2	3.5
Labour cost (additional cost for electrolytic reduction)	5.7	-	-	-
Waste treatment	-	6.9	8.8	-
Energy cost (¢ kg ⁻¹ U)	3.7	neg.	neg.	neg.
Catalyst costs (¢ kg ⁻¹ U) (capital charges on inventory)	-	-	-	0.8
Replacement cost (3 changes per 5 years)				2.5
Replacement cost (3 changes per year)				(9.2)
TOTAL COST (¢ kg ⁻¹ U)	90.0	21.5	34.6	6.2 (13.1)

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TABLE 8

SPECTROGRAPHIC ANALYSIS OF RUM JUNGLE LEACH LIQUOR,
URANYL CHLORIDE STRIP SOLUTION AND UF₄ PRODUCT

Element	Leach Liquor $\mu\text{g g}^{-1}$ (U basis)	UO ₂ Cl ₂ Solution $\mu\text{g g}^{-1}$ (U basis)	UF ₄ Product $\mu\text{g g}^{-1}$ (U basis)
Ag	100	<1	<1
Al	300,000	25	20
Cd	140	0.3	<0.5
Ca	790	15	<10
Cr	1,700	<5	<5
Cu	27,000	25	5
Fe	800,000	100	30
Mg	1,800,000	15	<5
Mn	760,000	<1	4
Mo	20,000	1	<1
Ni	6,400	5	4
Na	570,000	70	-
Zn	4,500	80	<10
B	500	0.6	0.5
Si	295,000	70	35

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TABLE 9
 COMPARISON OF PURITY OF UF₄ PRODUCTS

Element	UF ₄ from Rum Jungle leach liquor μg g ⁻¹ (U basis)	UF ₄ (after Takada et al. 1971) μg g ⁻¹ (U basis)
Ag	<1	<0.2
Al	20	5
Cd	<0.5	<0.1
Ca	<10	-
Cr	<5	4
Cu	5	5
Fe	30	25
Mg	<5	<1
Mn	4	1
Mo	<1	1
Ni	4	8
Na	-	-
Zn	<10	-
B	0.5	<0.1
Si	35	8

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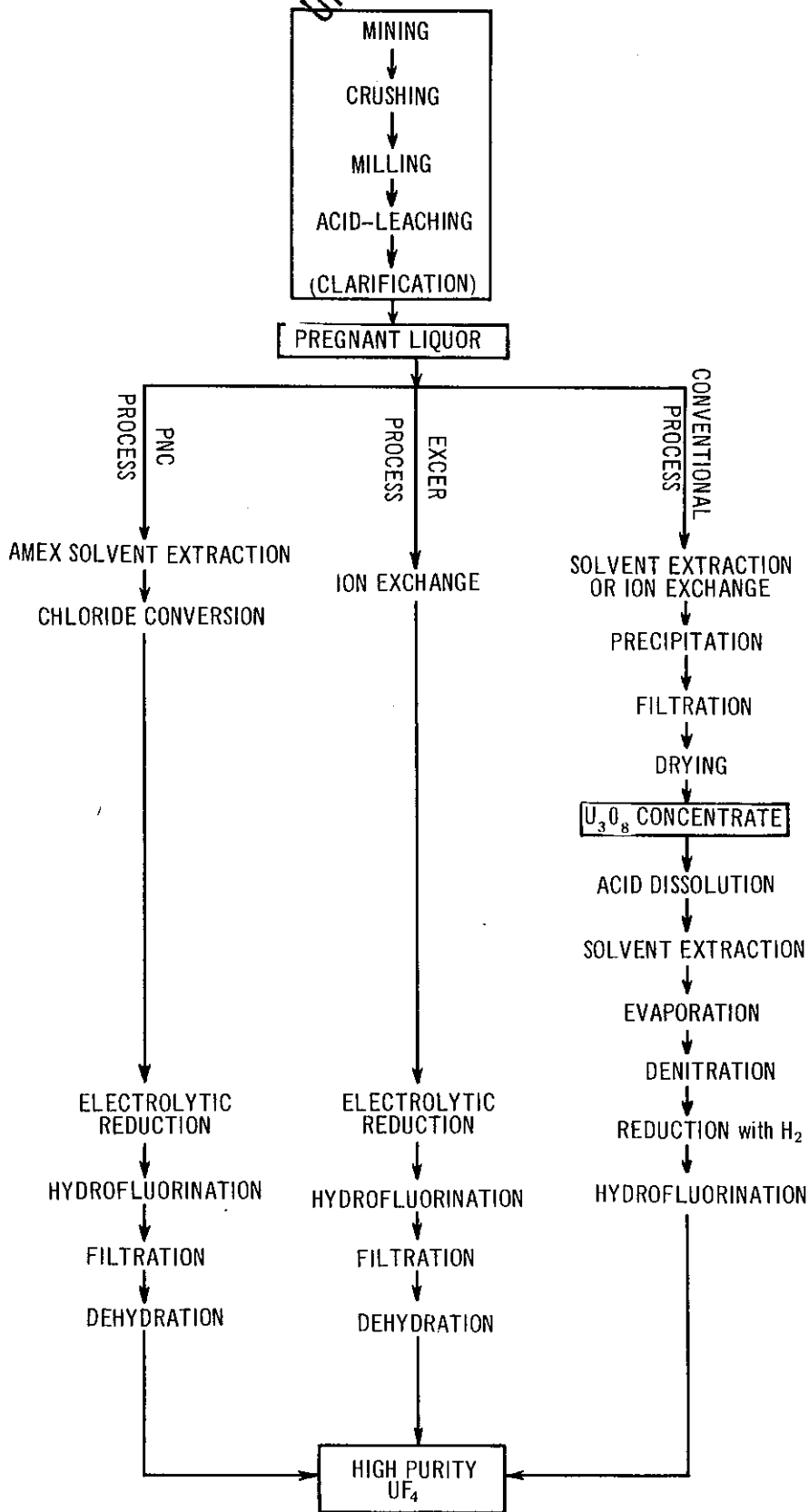


FIGURE 1. COMPARISON OF PNC PROCESS WITH EXCER AND COMMERCIAL CONVERSION PROCESSES

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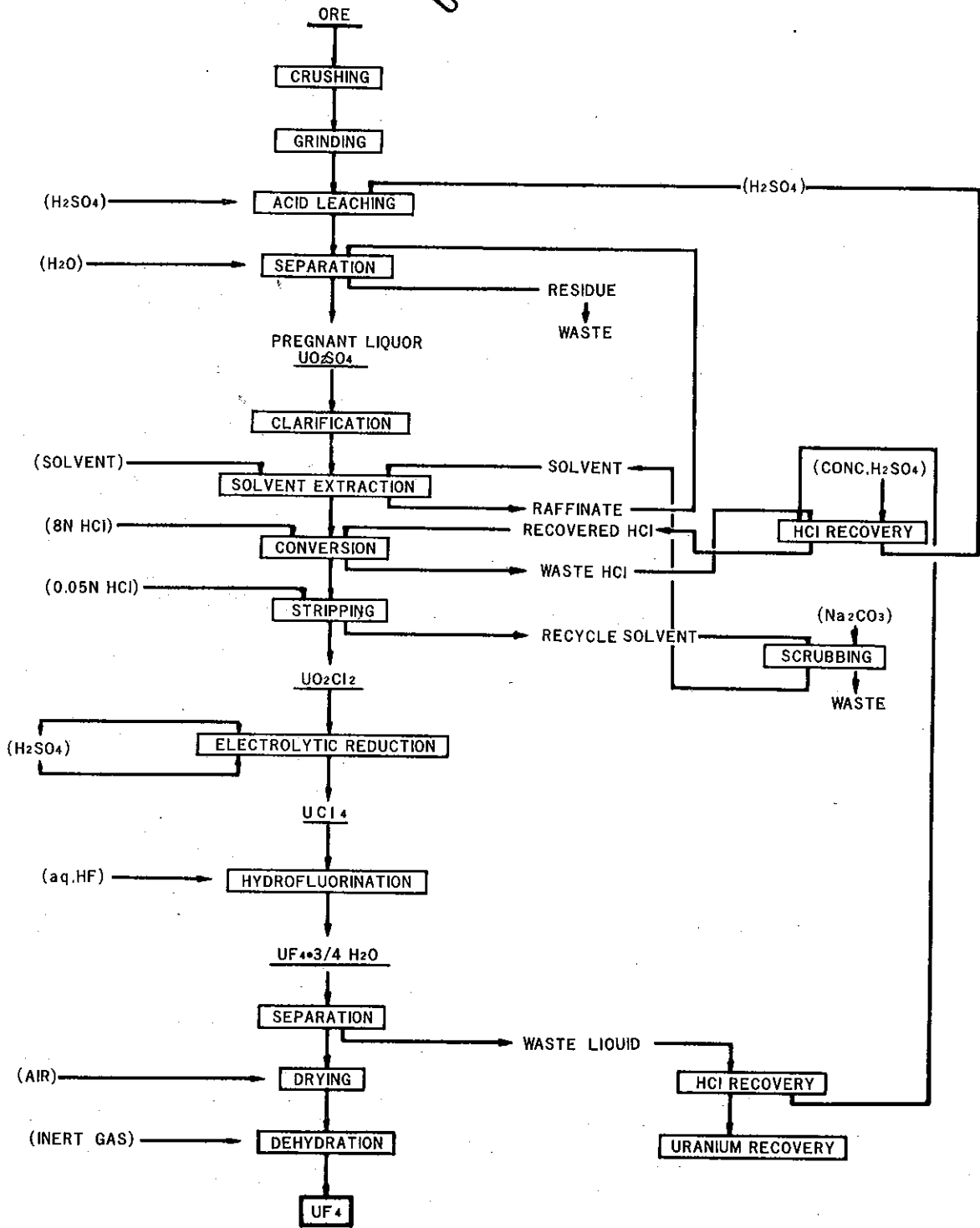


FIGURE 2. THE PNC PROCESS

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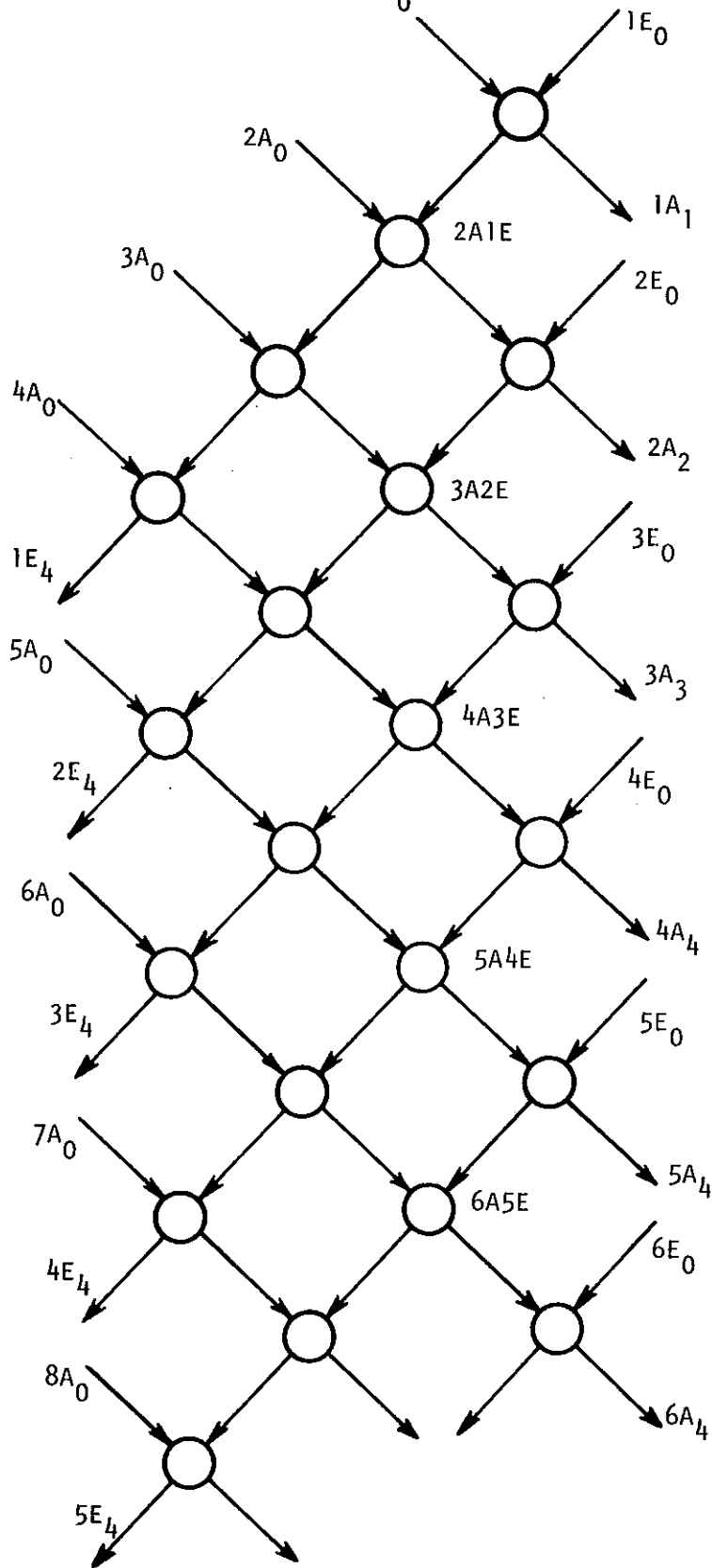


FIGURE 3. BATCHWISE SIMULATION OF A FOUR STAGE COUNTERCURRENT EXTRACTION CYCLE

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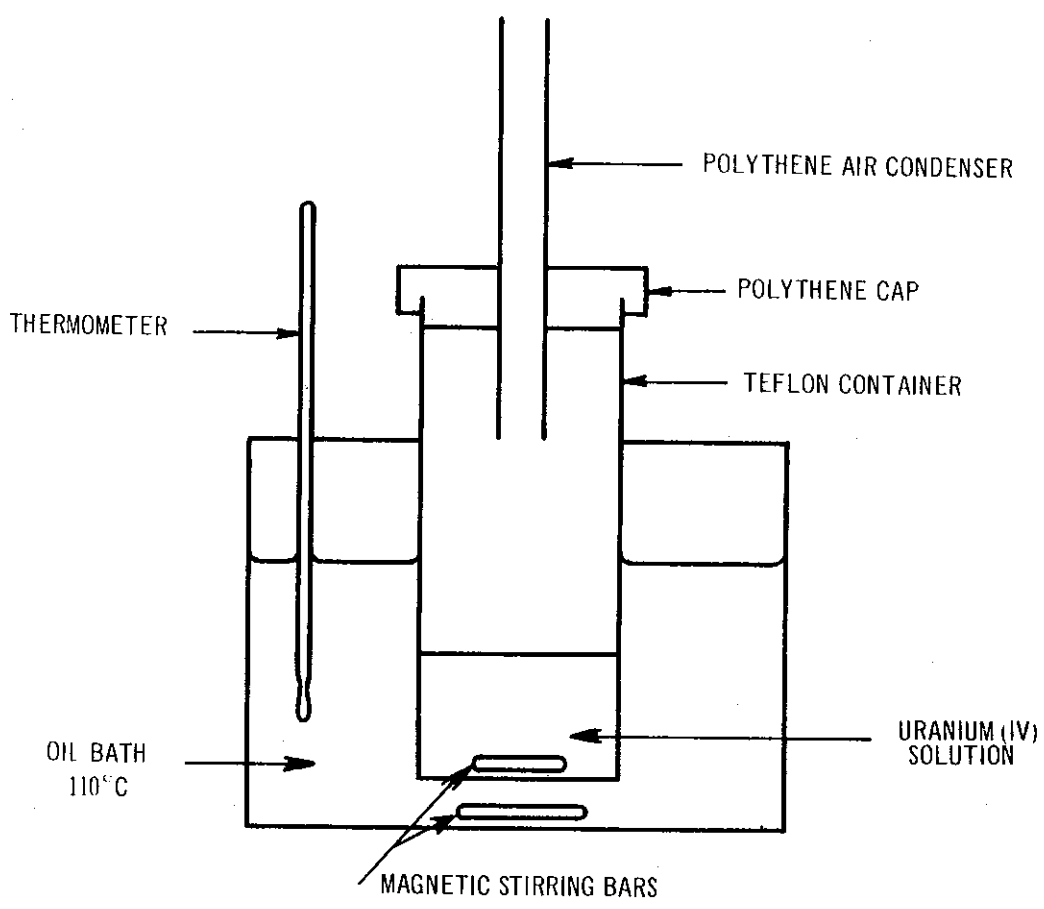


FIGURE 4. APPARATUS FOR UF_4 PRECIPITATION

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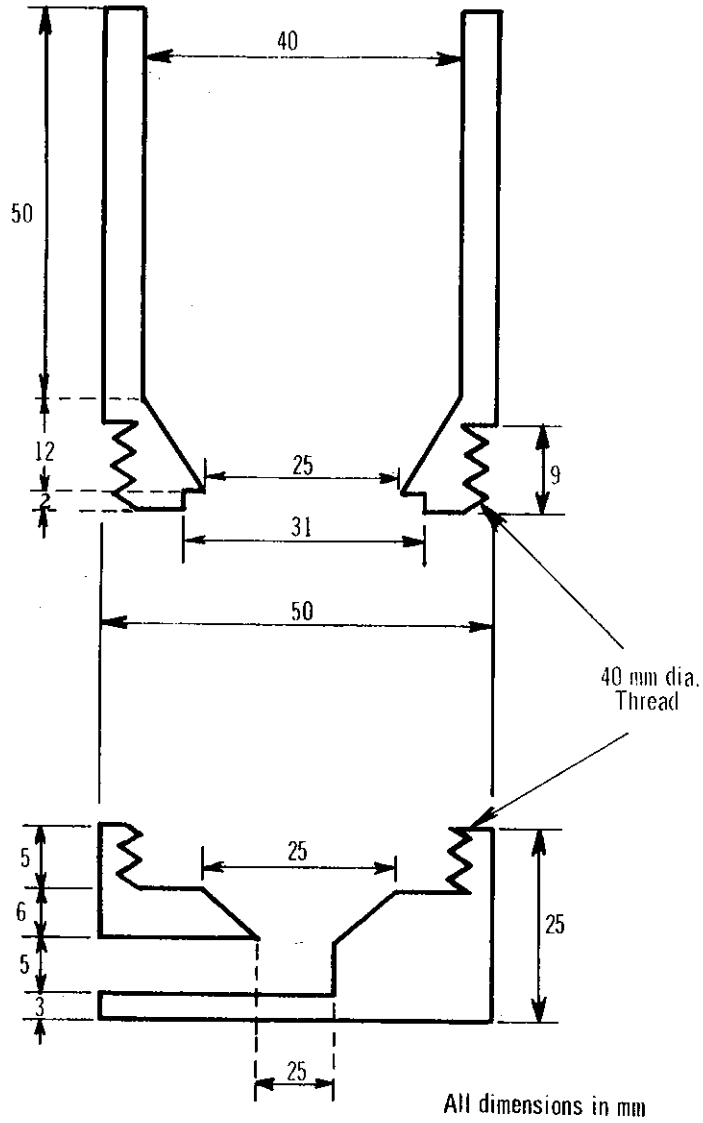


FIGURE 5. TEFLON FILTRATION APPARATUS

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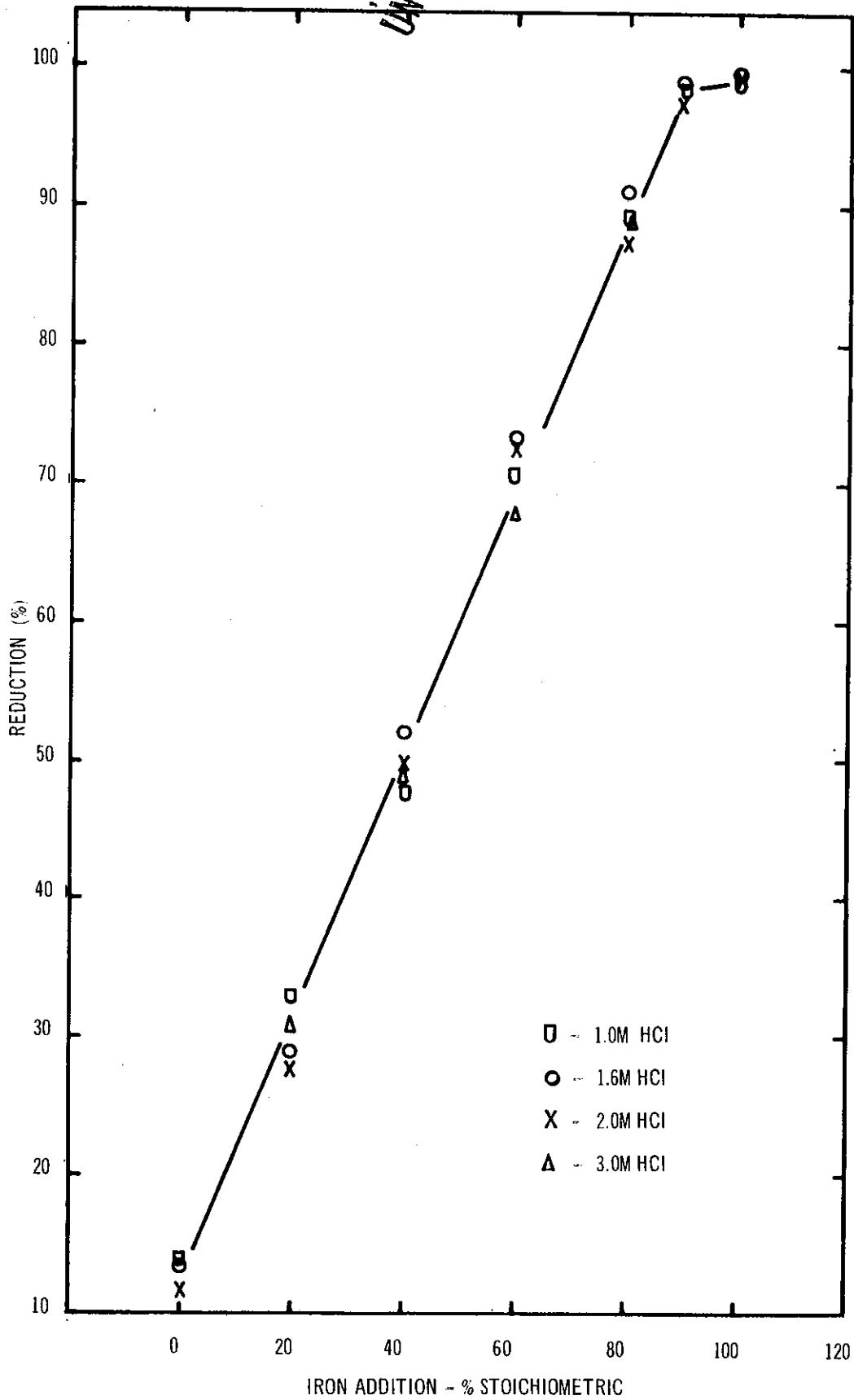


FIGURE 6. URANIUM REDUCTION AS A FUNCTION OF PER CENT STOICHIOMETRIC IRON

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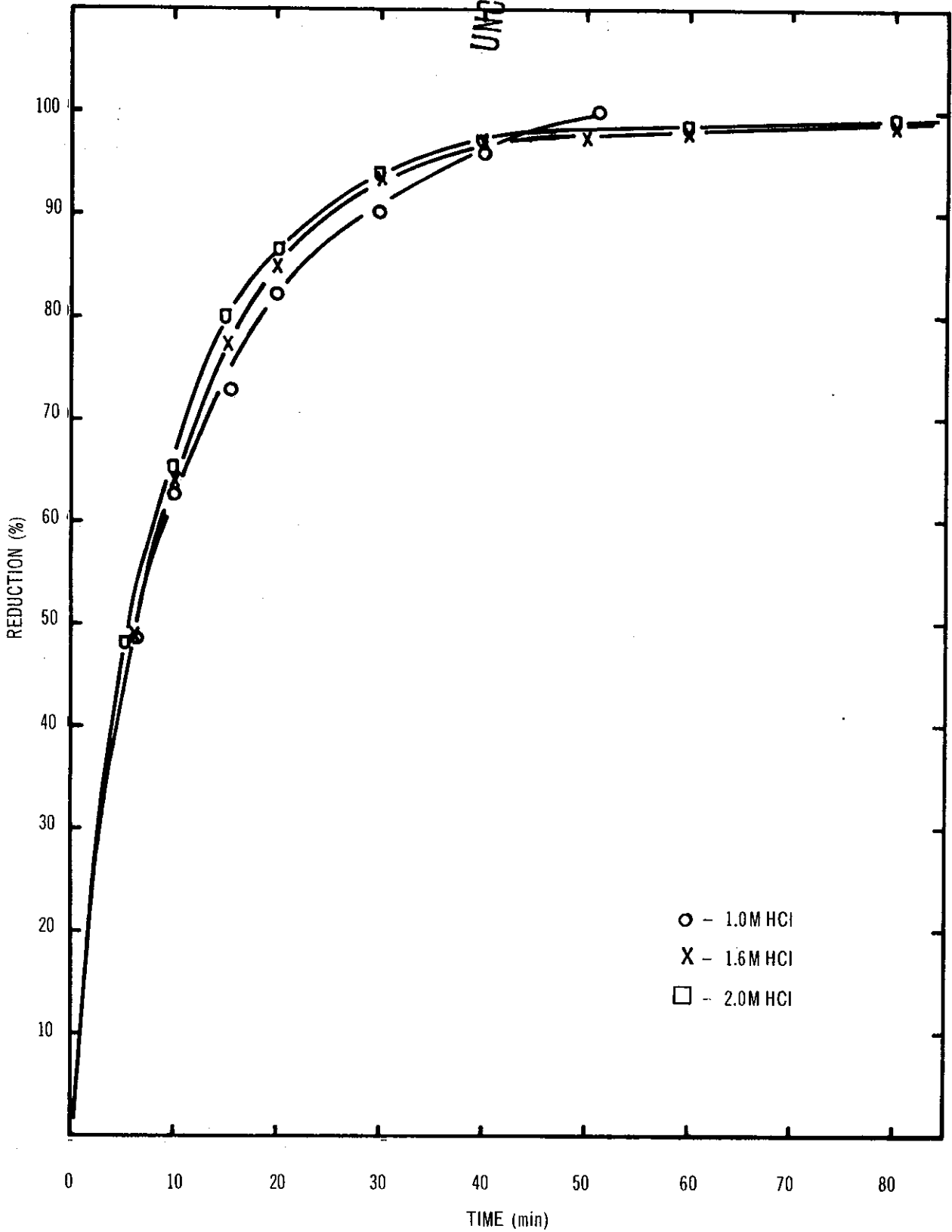


FIGURE 7. RATE OF URANIUM REDUCTION AS A FUNCTION OF HCl CONCENTRATION

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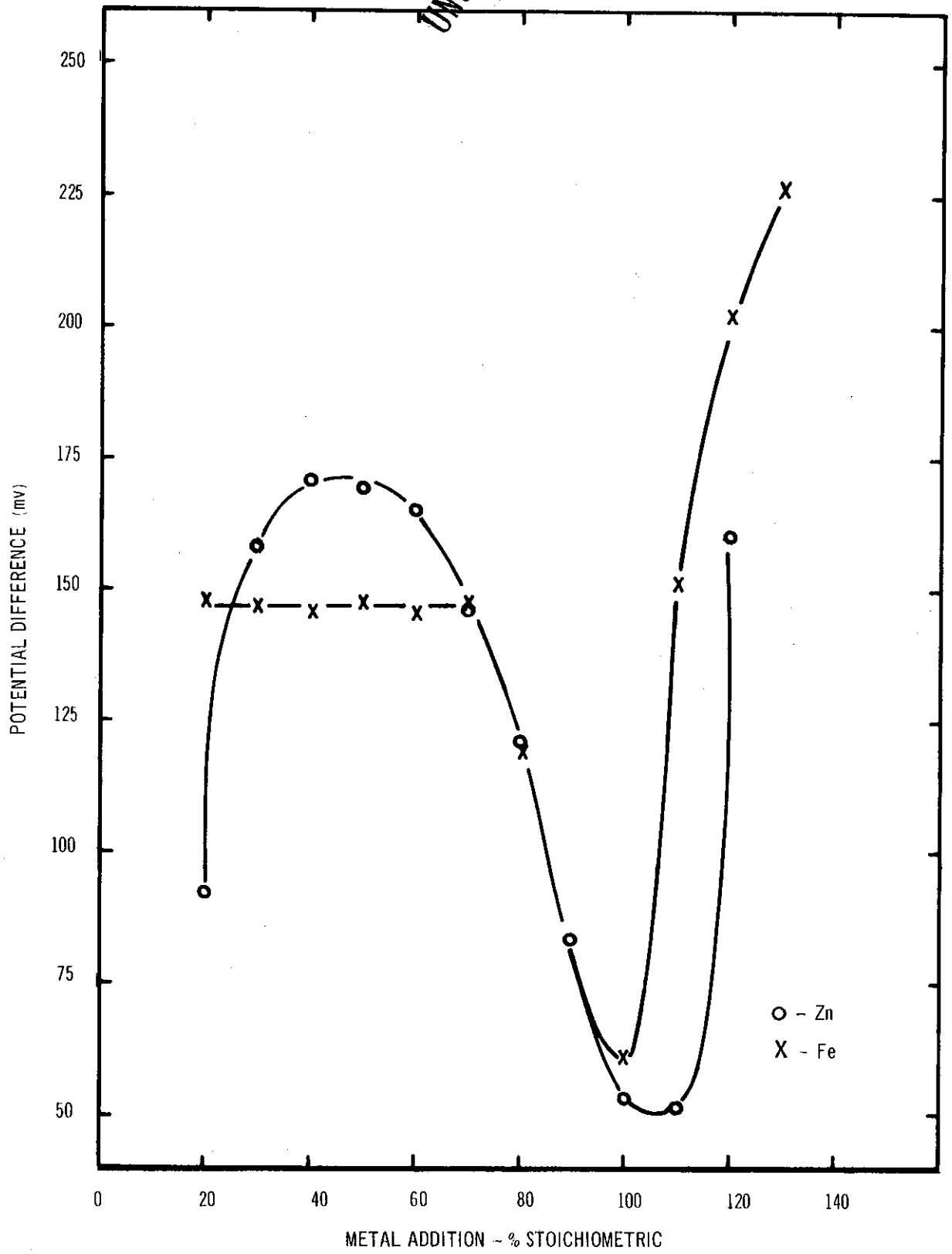


FIGURE 8. POTENTIAL DIAGRAM FOR URANIUM REDUCTION BY IRON AND ZINC

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