UCRL- 85032
PREPRINT

CONF-810519--1

MASTER

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This paper was prepared for submittal to
Workshop on Alternate Nuclear Waste Forms
and Interactions in Geologic Media
Gatlinburg, Tennessee

May 13-15, 1981

Lawrence Livermore Laboratory

THE APPLICATION OF SYNROC TO HIGH-LEVEL DEFENSE WASTES*

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ABSTRACT

The SYNROC method for immobilization of high-level nuclear reactor wastes is currently being applied to U.S. defense wastes in tank storage at Savannah River, South Carolina. The minerals zirconolite, perovskite, and hollandite are used in SYNROC D formulations to immobilize fission products and actinides that comprise up to 10% of defense waste sludges and coexisting solutions. Additional phases in SYNROC D are nepheline, the host phase for sodium; and spinel, the host for excess aluminum and iron.

Up to 70 wt% of calcined sludge can be incorporated with 30 wt% of SYNROC additives to produce a waste form consisting of 10% nepheline, 30% spinel, and approximately 20% each of the radioactive waste-bearing phases. Urea coprecipitation and spray drying/calcining methods have been used in the laboratory to produce homogeneous, reactive ceramic powders. Hot pressing and sintering at temperatures from 1000 to 1100°C result in waste form products with greater than 97% of theoretical density. Hot isostatic pressing has recently been implemented as a processing alternative.

Characterization of waste-form mineralogy has been done by means of XRD, SEM, and electron microprobe. Leaching of SYNROC D samples is currently being carried out. Assessment of radiation damage effects and physical properties of SYNROC D will commence in FY81.

INTRODUCTION

A considerable amount of research effort is currently being devoted to SYNROC applications for both commercial wastes and defense wastes. The focus of this presentation will be on high-level defense wastes, although I will be reviewing some of the work currently being done on civilian wastes. A synopsis of the presentation is as follows: First, I'll give an overview of SYNROC research as I know it. I will try to bring you up to date on SYNROC-related work in various universities and national laboratories. Second, I will present a brief overview of the nature of U.S. defense wastes. The major portion of the presentation will focus on the mineral waste form

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* Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-eng-48

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED development work being done at the Lawrence Livermore National Laboratory in the areas of powder preparation techniques, waste-form synthesis and characterization, leaching studies and, finally, some of our early thoughts on production technology schemes.

CURRENT SYNROC RESEARCH EFFORTS

SYNROC came on the scene in November, 1978, when it was introduced in a paper[1] by Professor A. E. Ringwood of the Australian National University. Ringwood's concept is a notable variation on the ceramic waste-form theme introduced earlier by Rustum Roy[2] and Gregory McCarthy[3] at Pennsylvania State University. During the past two years, a considerable amount of research and development has been done on SYNROC, and I will briefly review some of those efforts (Table 1).

At the Australian Atomic Energy Commission, Keith Reeve and his colleagues have been conducting waste-form synthesis studies on SYNROC C (both hot pressing and sintering), leaching studies, and studies of radiation effects[4]. They are also working on production technology aspects of SYNROC, focusing on uniaxial hot pressing.

At Australian National University, Professor Ringwood and his colleagues are working on waste-form "optimization," i.e., they are experimenting with various modifications of the SYNROC C and SYNROC D[5] formulations in order to get the best possible waste forms for commercial and defense applications. They are also doing radiation effects studies on natural zirconolite and perovskite and are thinking about various production technology schemes. Conceptual flow sheets for SYNROC processing are being evaluated, and I expect that a considerable effort will be devoted to that area of research during the next year. Professor Ringwood has recently published a paper which outlines his concept of a deep-hole waste repository[6].

At Argonne National Laboratory, Chris Kennedy[7] and Rich Arons are doing single-phase synthesis of hollandite, zirconolite, and perovskite as well as SYNROC C, and Kevin Flynn is doing leaching studies by means of neutron activation analysis. Bill Primak, who has been engaged in experimental research on radiation-effects in non-metallic inorganic solids for over three decades, will be involved in radiation damage studies of SYNROC phases.

At the Idaho Chemical Processing Plant (ICPP), they are looking at the potential application of SYNROC to some of their calcines, and have been doing waste-form synthesis, leaching, and characterization work.

At Los Alamos Scientific Laboratory, Frank Clinard's group is doing single-phase synthesis and radiation effects studies on the fluorite-type structures and zirconolite.

At North Carolina State University, Hayne Palmour III and his colleagues[8] are doing rate-control sintering, characterization of the sintered forms, and leaching studies.

At Oak Ridge National Laboratory, Jack Lackey, Pete Angelini, and Dave Stinton are doing production technology work in the application of sol gel techniques to SYNROC[9]. They are doing waste-form synthesis via the sol gel route and characterization of the waste forms by means of x-ray diffraction, microprobe analysis and autoradiography.

At Sandia Laboratories, they have been working on the titanate ceramic process for waste encapsulation for a number of years[10]. The phases that are produced from their titanate formulations are, in some cases, similar to the mineralogy of SYNROC. In addition to synthesis studies, they are also doing characterization of the microstructure, leaching studies and have been thinking about innovative ways to facilitate production technology. They are applying the titanate ceramic work to both commercial and defense wastes.

At Battelle Pacific Northwest Laboratories (PNL), they have done some early work in alternate waste-form synthesis and leaching, and more recently they have done radiation damage studies on synthesized zirconolite.

The University of Western Ontario personnel will present a paper at this symposium on the stability of perovskite in natural waters.

I have recently heard that Professor Don Lindsley, an experimental petrologist at SUNY, Stony Brook, will be doing phase equilibria work on SYNROC-type formulations.

Finally, at Lawrence Livermore National Laboratory, we are doing waste-form synthesis, characterization, and leaching. Production technology work is at the conceptual stage, and we are planning to study radiation effects in FY81. We have divided the effort into five tasks: waste form development and synthesis; characterization; stability assessment (leaching and radiation effects); ceramic processing; and production technology. We began our waste-form development work in July, 1979, and have progressed through the various SYNROC formulations during the past year. We began with SYNROC B (no radwaste), progressed to SYNROC C (the waste form for commercial radwaste applications), and are now working almost exclusively on SYNROC D (defense waste). A synopsis of the activities done in the five separate research and development areas under the LLNL program are given in Table 2.

U.S. DEFENSE WASTES

I will present a brief description of U.S. defense wastes for those who are not familiar with the particular characteristics of that material. High-level defense wastes are generated by (1) the production of plutonium and tritium for nuclear weapons work at Hanford, Washington, and Savannah River, South Carolina, and (2) by processing of spent naval reactor fuels at the Idaho Chemical Processing Plant in Idaho Falls. Current inventories total approximately 76 million gallons. The distribution of wastes among the four storage sites is given in Table 3. Defense wastes, as it exists in tank storage, is made up of three components: sludge, salt cake, and supernatant liquid. The sludge and salt cake result from a process by which the acid waste stream from the nuclear fuel reprocessing cycle is neutralized with NaOH. The sludge is the focus of interest in the waste-form development work because all of the radionuclides, with the exception of cesium, are strongly partitioned into that material. The processing of the sludge results in the encapsulation of the actinides and most fission products. Cesium is strongly partitioned into the supernatant liquid which is processed in a separate line initially, but the cesium is ultimately incorporated with the other radwaste into a single waste form. The defense wastes at the Savannah River Plant are scheduled to be the first wastes processed for permanent storage. Hanford and the ICPP are currently in the process of evaluating the potential application of alternate waste forms to their diverse waste inventory.

Defense waste sludge is a formidable material with which to work. Physically, it is the color of axle grease, has the consistency of mayonnaise and consists of approximately 95% fluid and 5% solids. Chemically, the material is diverse. Table 4A lists the major component compositions of specific tanks that have order-of-magnitude differences in iron, aluminum, uranium and others. Also listed is the composite or average composition for the total inventory. Minor element chemistry is also varied and diverse. A waste form that is to be applied to defense wastes must have the flexibility to incorporate the extreme differences in sludge composition.

Strontium is the principal radionuclide in sludge, followed by cesium, ruthenium and europium. There is a minute amount of cesium in the sludge. The level of cesium in the supernatant liquid is equivalent to the strontium level in the sludge. Alpha activity level is quite low (Table 4B).

SYNROC MINERALOGY

The principal minerals in SYNROC formulations are titanates; hollandite ($BaAl_2Ti_6O_{16}$), zirconolite ($CaZrTi_2O_7$) and perovskite ($CaTiO_3$). All three are made up of Ti-O octahedra networks. In SYNROC D formulations, nepheline ($NaALSiO_4$) and spinel ($R_2^{+++}O_3 \cdot R^{++}O$) are additional phases. Hollandite is the principal host for Cs in SYNROC, Sr goes into solid solution in perovskite and the rare earths and actinides are partitioned equally between perovskite and zirconolite. Uranium is partitioned into zirconolite (Fig. 1). The small amount of cesium that is present in the sludge enters into solid solution in nepheline. The theoretical density of SYNROC D formulations ranges from about 4.1 to 4.5 g/cc, depending on the spinel composition.

POWDER PREPARATION TECHNIQUES

Compositionally homogeneous and chemically reactive starting powders are necessary in order to sinter/hot press ceramics to full density at temperatures below the solidus. Three techniques have been used at LLNL to prepare reactive starting powders. The first technique is that of simply grinding and mixing oxides, hydroxides, and salts. The principle mode of mixing this material has been in a "vibro-energy" mill consisting of small alumina or zirconia pellets in a can containing a powder slurry. Vibratory motion causes the pellets to rub against one another and, in turn, grind and mix the powder.

We have made ample use of the urea coprecipitation technique developed by Tom Quinby[1] at ORNL. We have made about twenty-five different batches of starting material by means of the urea method. The principal advantage of the method is that homogeneous powders with very high surface areas are produced by the technique. The basis and mechanism of urea coprecipitation is given in diagrammatic form in Fig. 2.

The method we are currently using to do all of our powder preparation is spray drying (Fig. 3). Our reason for going to spray drying is that the process more closely simulates the production technology schemes that will be used in large-scale sludge processing. Powder properties have not been compromised for the sake of engineering simulation, however. The spray-dry technique has been found to produce very reactive powders. The highest temperature attained in the spray dryer is approximately 300°C, therefore batch calcining is done subsequent to drying.

Reactive powders with high surface areas promote sintering at low temperatures and tend to produce dense, homogeneous ceramic end-products. The data in Fig. 4 represent measured surface areas for a variety of SYNROC powder preparations as a function of calcining temperature. It appears that sintering begins to take place when powders are heated to 600°C. X-ray diffraction data for a sample of SYNROC B powder calcined at temperatures between 600°C and 1000°C reveals that mineral phases begin to develop in the vicinity of 700°C (Fig. 5)[12]. All of the principal SYNROC phases have been synthesized at 1000°C. Hot pressing or sintering to higher temperatures promotes grain growth and results in densification of the waste form. Optimum calcination temperatures for SYNROC formulations ranges from 650°C to 900°C.

WASTE-FORM SYNTHESIS

The experimental procedure for SYNROC waste-form synthesis is shown in Fig. 6. SYNROC D formulations contain up to 70 wt% sludge and 30 wt% SYNROC additives, i.e., the oxide components that bring about the desired phase assemblage. Defense waste sludges contain up to 10 wt% radwaste components, therefore, the maximum radwaste loading in SYNROC D is 7%. Cold pressing is a necessary step prior to sintering and hot isostatic pressing. Calcined powders go directly into the dies in the uniaxial hot-pressing operation.

Most of the waste-form synthesis work at LLNL has been done by uniaxial hot pressing, either in graphite dies or in metal (Ni or Fe) capsules (Fig. 7)[13]. The purpose of using the metal capsules (and adding metal powder to the formulation) is to control the redox state during hot pressing. It is desirable on the basis of equilibria considerations, to have a ferric/ferrous ratio near unity and this is accomplished in the vicinity of the nickel-nickel oxide buffer; thus the use of capsules and metal powder. Differential thermal analysis indicates that the solidus for SYNROC D formulations with composite waste is near 1125°C. Hot-pressing parameter studies have been carried out at temperatures between 950°C and 1150°C (Fig. 8). Each data point in Fig. 8 represents the extent of densification that is attained at the end of a one-hour duration in the hot press. It is clear that SYNROC D formulations can be pressed to near theoretical density at temperatures as low as 1050°C. The SYNROC C data in Fig. 9 suggests that powders of a similar composition, but prepared by means of different techniques, have similar densification characteristics during hot pressing. This is not a surprising result in that the urea coprecipitation and the spray drying techniques both produce powders with surface areas in excess of 100 m^2/gram.

PRODUCTION TECHNOLOGY

It was mentioned earlier that the sludge contains the bulk of the radwaste components of defense wastes and the supernatant liquid contains the cesium. The reference flow sheet for the processing of Savannah River Plant wastes[14] defines a sludge-processing stream and a supernatant liquid-processing stream which merge so that all of the radwaste components are eventually encapsulated in the same waste form (Fig. 10). The specific makeup of SYNROC D is determined on the basis of the radwaste and inert components present in defense wastes. A SYNROC formulation based on SRP composite sludge is given in Table 5. The cesium host, hollandite, is presynthesized and added to SYNROC D calcine prior to hot pressing of the composite form.

A conceptual flow sheet for uniaxial hot pressing of SYNROC D is shown in Fig. 11. The important aspects of the flowsheet are as follows: (1) the SYNROC additives are prepared outside of the hotcell, (2) a spray calciner or, alternatively, a spray dryer coupled with a rotary kiln are potential processes for the mechanism for decomposition of sludge and additives, and (3) a presynthesized Cs-bearing waste form is added prior to hot pressing. Fig. 12 depicts the type of "stacking" experiments that have been carried out at LLNL. Another alternate method that is currently being investigated represents a variation of the process presented in Fig. 12. Instead of hot pressing to final denisty, the successive disks in the stack are "warm" pressed in order to achieve a high initial density. The capsule would subsequently be hot isostatic pressed to full density. A large research effort in the area of large scale processing will be done at LLNL during FY81.

LEACHING

In consideration of the manner in which SYNROC D will be formulated, the leaching data is presented in terms of the respective host materials. The data presented in Table 6 represents the componenets of the SYNROC D matrix, i.e., the radwaste incorporated in perovskite, zirconolite and the small amount of cesium present in nepheline. The data in Fig. 13 represents the leaching characteristics of single phase Cs-bearing hollandite[15]. The leaching characteristics of the combined products are currently undergoing evaluation and will be available in early FY81.

Two types of leaching studies are currently being done at LLNL. Scoping or reconnaissance studies are being done in a static mode in Teflon containers at temperatures ranging from 75°C to 150°C for short periods of time. This method is in accordance with recommendations of the Materials Characterization Center (MCC) at PNL. More comprehensive studies are being done by means of the continuous flow leaching system at 25°C and 75°C for periods up to two months (Fig. 14). The duration of the continuous flow experiments has been limited by the sensitivity of analytical techniques used on the leachates. Tracer doping of SYNROC samples will be done in FY81 in order to increase analytical sensitivity.

DISCUSSION

POHL: I understood, from the introduction, that there is a great variety of chemical compositions in the Savannah River sludges. The conceptual flow sheet that you showed at the end did not seem to take that into consideration. Are you planning to make one grand mixture and then use that, or do you plan to use different mixing ratios and processes for the different compositions to be determined as you start going from one tank to the next tank?

TEWHEY: The experimental work we have conducted thus far has focused on the composite sludge composition. I have an extra slide (Fig. 14) which depicts the phase equilibria for SYNROC D for three sludge compositions in terms of the three principal compoents, Al_2O_3, FeO, and TiO_2. The principal phases in the SYNROC D matrix: perovskite, zirconolite, nepheline and spinel are plotted in terms of their composition with respect to aluminum, iron and titanium. Note that the composition of the zirconolite, perovskite and nepheline show very little variation from one bulk composition to another. On the other hand, the composition of the spinel phase, which comprises up to 50 wt% of the waste form, varies considerably in the three ternary diagrams. Spinel is the "forgiving" phase in SYNROC D, that is, the additive stream does not have to be "fine-tuned" for each sludge composition. We predict that an additive stream that is variable within narrow limits will be adequate to produce the desired SYNROC assemblage in the three sludge compositions. The considerable differences in sludge composition will influence the spinel composition, which will vary from being Al-rich to Fe-rich.

WITTELS: In the graphs you showed on leaching, the leach rate of hollandite tends to reduce as a factor of time. What did you measure, and what is the physical picture you ascribe to this decrease? I do not have a physical picture of why this rate should decrease so dramatically, if you have a through-flow system.

TEWHEY: Our method of analysis in the continuous-flow leaching experiments is to measure the composition of the leachate subsequent to it being in contact with the waste form. Samples are collected downstream from the sample holder and analyzed by means of XRF, ICP or INAA. The initial high leach rate is probably due to the material leached from surfaces and grain boundaries.

The leach rate that we are trying to determine is the rate that is measured thirty or forty days after the experiment starts. Up to now, we have had to stop our continuous-flow experiments prior to the time when the leach rate are expected to level out. Tracer loading of SYNROC samples will enable us to carry out longer leach experiments and to determine whether the leach rate levels off in the 10^{-9} or 10^{-10} region of the plot.

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FIGURE CAPTIONS

Fig. 1. The crystal structure and principal radwaste substitutions of SYNROC minerals.

Fig. 2. Schematic representation of the methodology and processing temperature of the urea coprecipitation method for the production of ceramic powders.

Fig. 3. Schematic of the laboratory-scale spray dryer used for the production of ceramic powders.

Fig. 4. Plot of measured surface area as a function of calcining temperature of SYNROC powder preparations made by urea coprecipitation and spray drying techniques.

Fig. 5. X-ray diffraction patterns for a SYNROC B formulation as a function of calcining temperature. A pyrochlore-type phase forms at 700°C and has nearly disappeared at 1000°C SYNROC phases are synthesized at 900°C. Powder was made by the urea coprecipitation method.

Fig. 6. Experimental procedure for the hot pressing/sintering of SYNROC D formulations with U.S. defense wastes. Bar on SEM photograph of microstructure is 10 um.

Fig. 7. Schematic of uniaxial resistance hot press for processing SYNROC D in metal capsules. The liner is not required when operating at temperatures below 1200°C.

Fig. 8. Results of uniaxial hot pressing parameter study of SYNROC D formulation produced by means of urea coprecipitation. Each data point represents the extent of densification after one hour at tmperature and pressure. The SYNROC D consists of 69 wt% simulated defense waste sludge (composite composition) and 31 wt% SYNROC additives.

Fig. 9. Densification plots versus time for uniaxial hot pressing of SYNROC C formulations made by means of various powder preparation techniques.

Fig. 10. Reference flowsheet for the processing of Savannah River Plant high-level defense wastes.

Fig. 11. Conceptual flowsheet for SYNROC processing utilizing uniaxial hot pressing.

Fig. 12. The sequence depicts the hot pressing steps in the production of a "stacked" monolith of a ceramic waste form.

Fig. 13. Leaching rate versus time for Cs-bearing hollandite in the continuous-flow leaching system. Leaching temperatures were 25°C and 75°C, flow rate was 30 ml/day and leach solutions were distilled water and a 0.03N $NaHCO_3$ solution. Except for the earliest samples, no temperature effect on leach rate was noticed.

Fig. 14. Diagram of the continuous-flow leaching system as set up for leaching of SYNROC samples.

Fig. 15. Phase compositions for minerals in SYNROC D for three sludge compositions. Spinel (S) shows evidence of being a "forgiving" phase, i.e., the composition varies significantly with bulk composition.

TABLE 1.
OVERVIEW OF CURRENT SYNROC RESEARCH

INSTITUTION	RESEARCH AREA
AUSTRALIAN ATOMIC ENERGY COMMISSION	o WASTE FORM SYNTHESIS o LEACHING o RADIATION EFFECTS o PRODUCTION TECHNOLOGY
AUSTRALIAN NATIONAL UNIVERSITY	o WASTE FORM "OPTIMIZATION" o RADIATION EFFECTS o PRODUCTION TECHNOLOGY o REPOSITORY DESIGN
ARGONNE NATIONAL LABORATORY	o SINGLE PHASE SYNTHESIS o LEACHING o RADIATION EFFECTS
IDAHO CHEM. PROC. PLANT	o WASTE FORM APPLICATION
LOS ALAMOS SCIENTIFIC LABORATORY	o SINGLE PHASE SYNTHESIS o RADIATION EFFECTS
NORTH CAROLINA STATE UNIVERSITY	o RATE-CONTROLLED SINTERING o CHARACTERIZATION o LEACHING
OAK RIDGE NATIONAL LABORATORY	o PRODUCTION TECHNOLOGY (SOL GEL) o WASTE FORM SYNTHESIS o CHARACTERIZATION (AUTORAD.)
SANDIA	o TITANATE CERAMICS
BATTELLE (PNL)	o WASTE FORM SYNTHESIS o LEACHING o RADIATION EFFECTS
UNIVERSITY OF WESTERN ONTARIO	o PHASE STABILITY IN AQUEOUS SOLUTION
STATE UNIVERSITY OF NEW YORK AT STONY BROOK	o MINERAL SYNTHESIS o PHASE EQUILIBRIA
LAWRENCE LIVERMORE NATIONAL LABORATORY	o WASTE FORM SYNTHESIS o LEACHING o RADIATION EFFECTS o PRODUCTION TECHNOLOGY

TABLE 2

MINERAL WASTE FORM DEVELOPMENT PROJECT

LAWRENCE LIVERMORE NATIONAL LABORATORY

WASTE FORM DEVELOPMENT	WASTE FORM CHARACTERIZATION	STABILITY ASSESSMENT	CERAMIC PROCESSING	PRODUCTION TECHNOLOGY
• POWDER PREP	• OPTICAL	• ACCEL. LEACH	• PROCESS DEV.	• ENGINEERING ASSESSMENT
• HOT PRESSING	• XRD	• CONTINUOUS FLOW LEACH	• SCALE UP	• ENGINEERING DEVELOPMENT
• SINTERING	• XRF	• RADIATION EFFECTS	• HOT CELL	• QUALITY ASSURANCE OF THE WASTE FORM
• HOT ISOSTATIC PRESSING	• SEM	• PHYS. PROPS.	• TRACER LOADING	
• PHASE EQUIL.	• MICROPROBE	• LEACH MECHANISMS	• SYNROC C	
	• STEM			

TABLE 3.
CURRENT INVENTORIES OF U.S. DEFENSE WASTES

	10^6GALS	10^6CURIES	10^6GALS SLUDGE
o HANFORD	50	540	11
o SAVANNAH RIVER	22	570	3
o IDAHO FALLS	3	85	*
o WEST VALLEY	1	65	.03
	76	$1.2x10^9$	14+

FOR COMPARATIVE PURPOSES, THE CURRENT INVENTORY OF U.S. COMMERCIAL WASTES (SPENT FUEL) IS $1.9x10^9$ CURIES.

*200 CU. YARDS OF ICPP WASTES EXIST AS DRY CALCINE POWDER.

TABLE 4A

MAJOR COMPONENTS IN SIMULATED SRP WASTE CALCINES

Component	High Fe	Composite	High Al
Fe_2O_3	53.17	36.13	5.32
Al_2O_3	4.89	28.26	76.05
MnO_2	3.56	9.94	4.37
U_3O_8	12.34	3.26	1.28
CaO	3.62	2.69	0.35
NiO	9.08	4.47	0.78
SiO_2	0.40	0.85	0.56
Na_2O	4.52	5.08	1.96
Na_2SO_4	<0.50	0.93	<0.50
Ion-Siv IE-95*	8.82	8.93	9.33

*Mixture of $CaAl_2Si_4O_{12}\cdot 6H_2O$ and $(NaKCa)_3Al_3SiO_{24}\cdot 8H_2O$

TABLE 4B

RADIONUCLIDES IN WASHED, DRIED SLUDGES

mCi/g

	Tank 5	Tank 7	Tank 13	Tank 15
^{90}Sr	74.7	27.0	15.5	25.6
^{144}Ce	4.8	0.2	2.0	16.9
^{106}Ru	2.7	1.4	0.4	1.7
^{154}Eu	0.5	-	0.3	1.2
^{137}Cs	1.3	1.3	0.3	0.1
Gross α	0.1	0.1	0.3	0.1

Source: Stone, J. A. et al, (1976), Sampling and Analysis of SRP High Level Wastes.
SR Publication DP-1399.

TABLE 6.

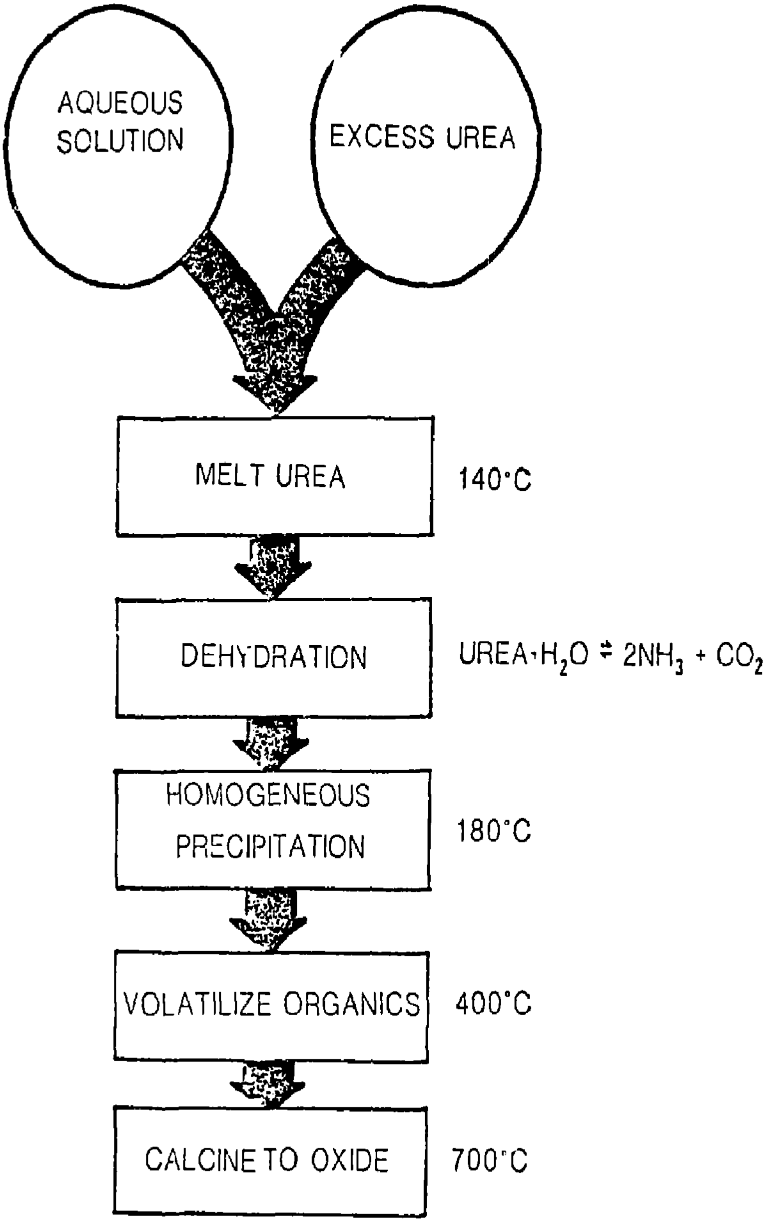
LEACHING RESULTS FOR SYNROC D WITH Cs HOLLANDITE ADDITION

Leaching conditions:
300°C, 1kb, 1 day, distilled water.
Results expressed in terms of g/SYNROC/cm^2 · day.

Al	5.9×10^{-7}
Ca	9.0×10^{-9}
Ce	ND
Fe	3.2×10^{-9}
Mn	7.9×10^{-11}
Na	3.8×10^{-5}
Ni	ND
Si	9.0×10^{-8}
Sr	ND
Ti	1.2×10^{-10}
U	ND
ZR	ND
Cs	8.2×10^{-6}
Gd	ND

Figure 1

UREA COPRECIPITATION METHOD



(QUINBY, 1978, ORNL)

Figure 2

SPRAY DRY METHOD

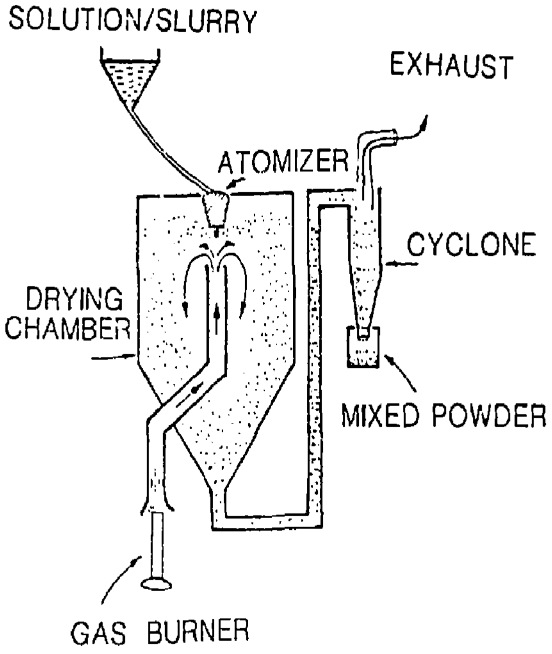


Figure 3

SURFACE AREA VERSUS CALCINATION TEMPERATURE
FOR SYNROC POWDER PREPARATIONS

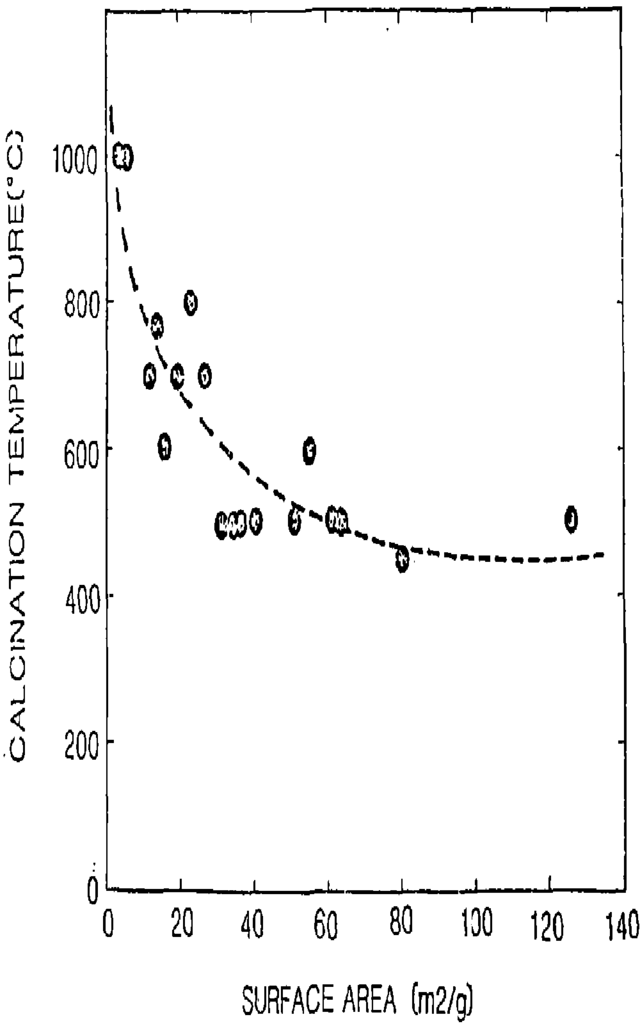


Figure 4

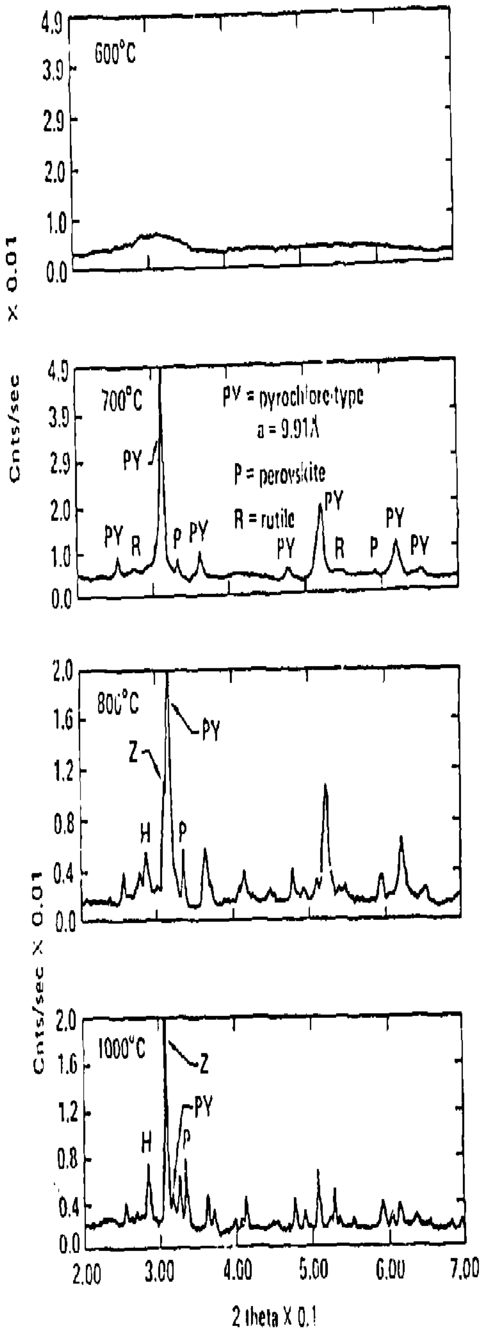
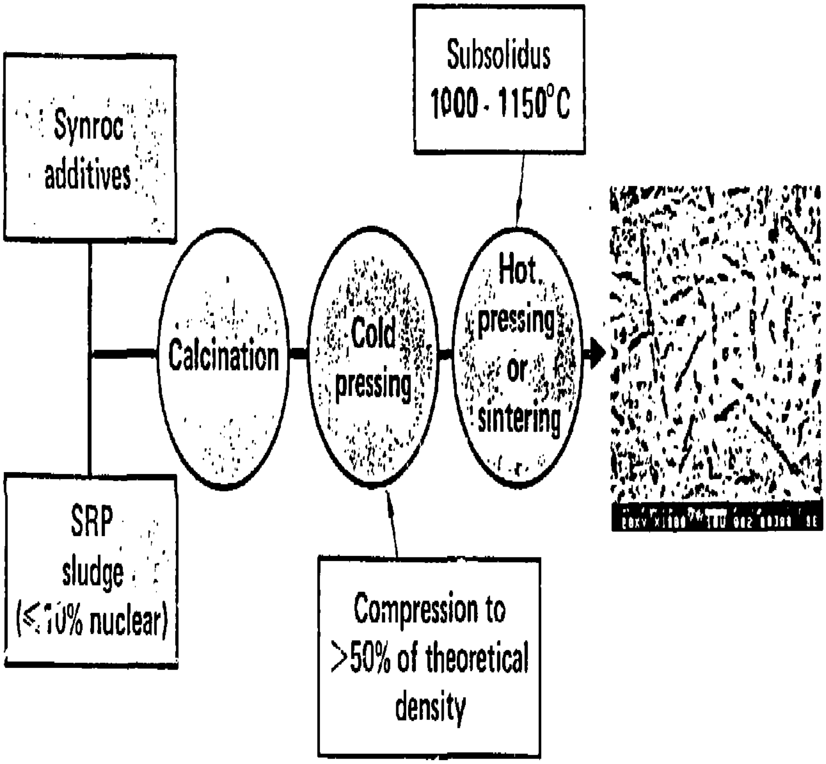

600°C
4.9
3.9
2.9
2.0
1.0
0.0
X 0.01
Cnts/sec
700°C
PY = pyrochlore-type
a = 9.91Å
P = perovskite
R = rutile
PY
PY
R
P
PY
PY
PY
R
P
PY
PY
800°C
Z
PY
H
P
2.0
1.6
1.2
0.8
0.4
0.0
Cnts/sec X 0.01
1000°C
Z
PY
H
P
2.00
3.00
4.00
5.00
6.00
7.00
2 theta X 0.1

Figure 5

EXPERIMENTAL PROCEDURE



Synroc additives

SRP sludge (≤10% nuclear)

Calcination

Cold pressing

Compression to >50% of theoretical density

Hot pressing or sintering

Subsolidus 1000 - 1150°C

Figure 6

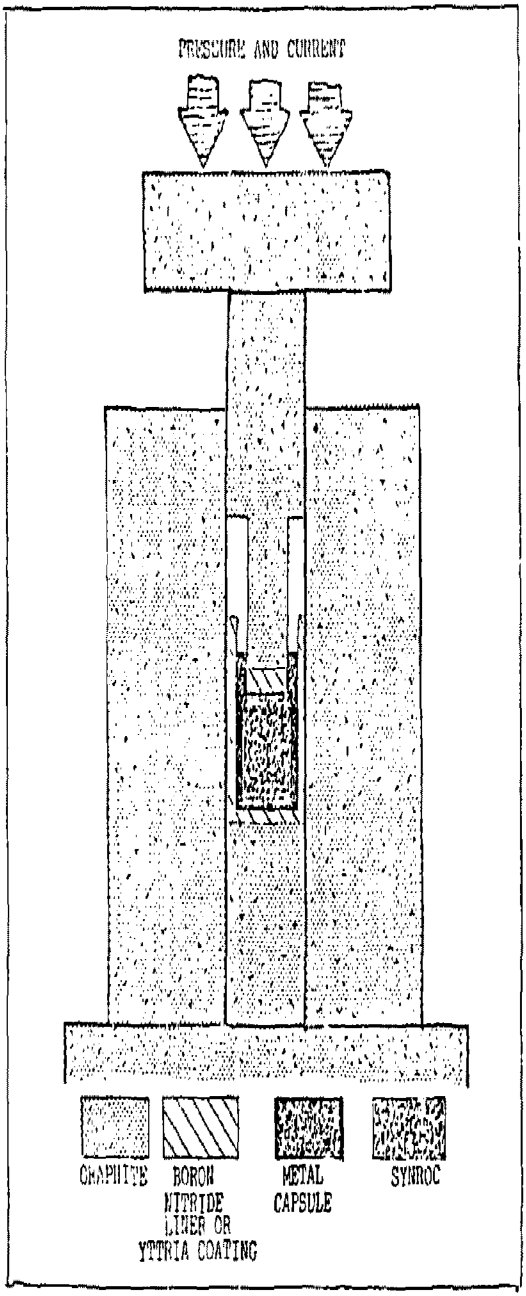

PRESSURE AND CURRENT
GRAPHITE
BORON NITRIDE LINER OR YTTRIA COATING
METAL CAPSULE
SYNROC

Figure 7

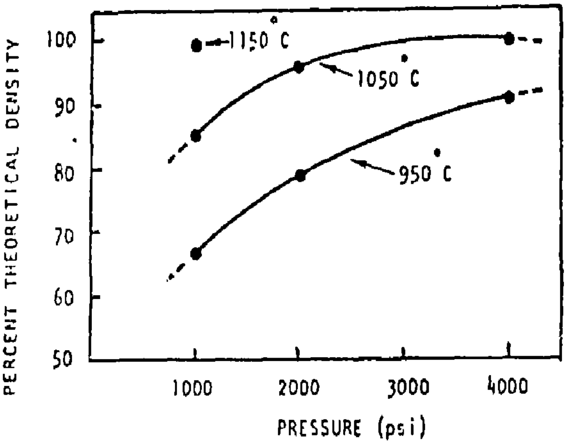


Figure 8

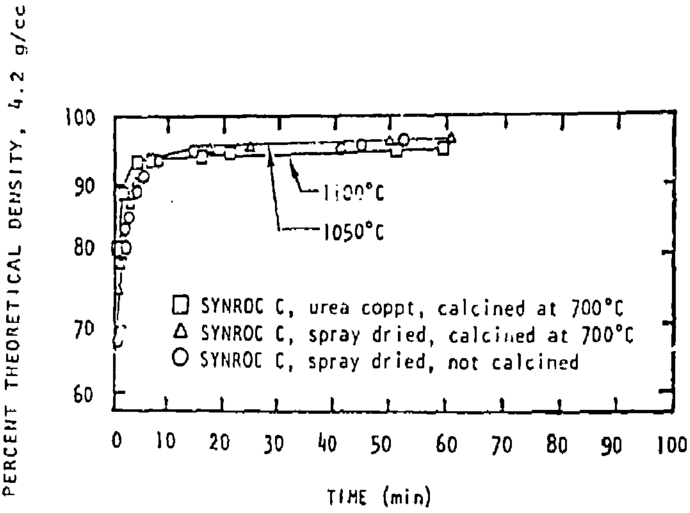


Figure 9

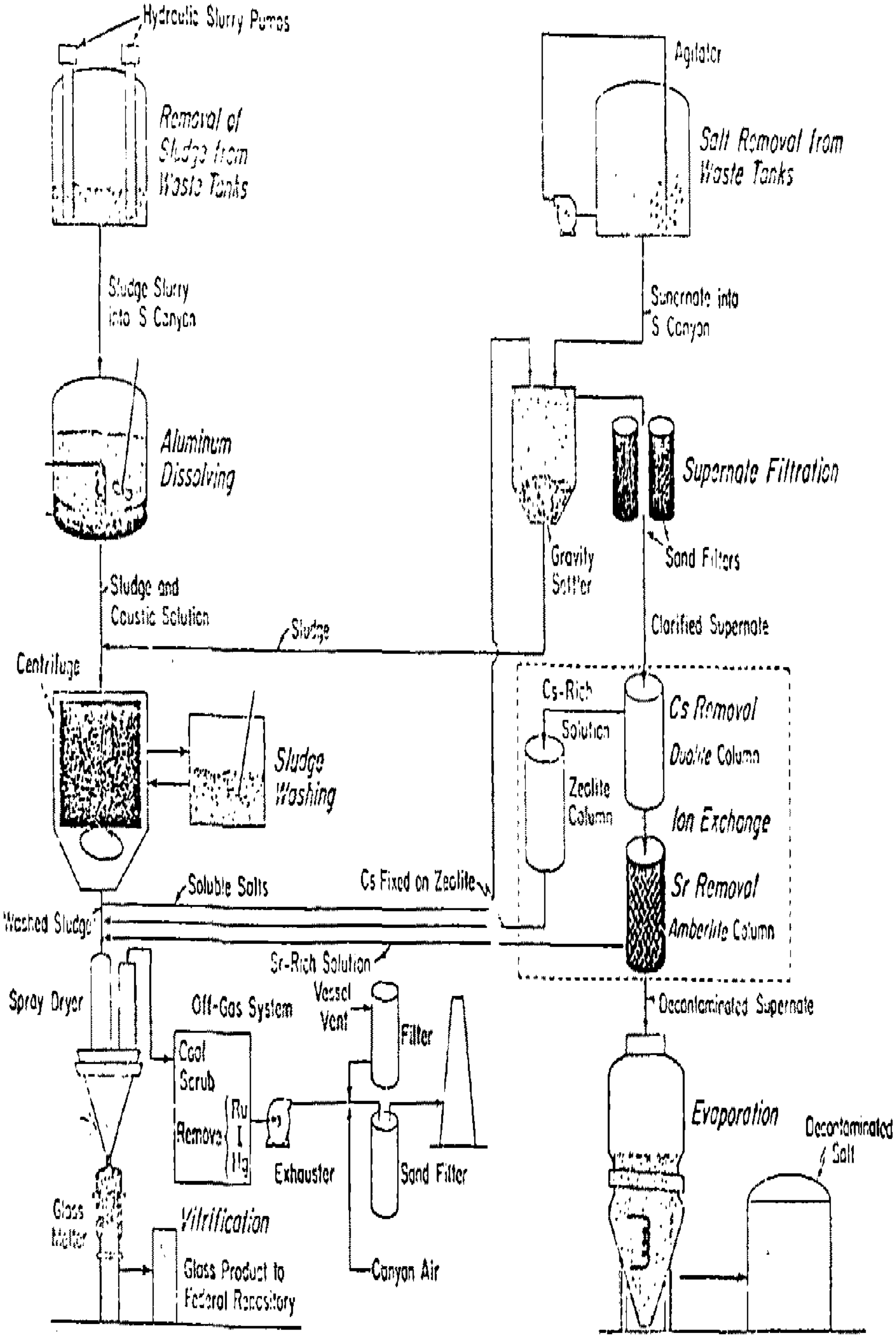

Hydraulic Slurry Pumps
Removal of Sludge from Waste Tanks
Agitator
Salt Removal from Waste Tanks
Sludge Slurry into S Canyon
Supernate into S Canyon
Aluminum Dissolving
Supernate Filtration
Gravity Settler
Sand Filters
Sludge and Caustic Solution
Sludge
Clarified Supernate
Centrifuge
Cs-Rich Solution
Cs Removal
Duolite Column
Zeolite Column
Sludge Washing
Ion Exchange
Sr Removal
Amberlite Column
Soluble Salts
Cs Fixed on Zeolite
Washed Sludge
Sr-Rich Solution
Decontaminated Supernate
Spray Dryer
Off-Gas System
Vessel Vent
Filter
Cool
Scrub
Remove
Ru
I
Hg
Exhauster
Sand Filter
Evaporation
Decontaminated Salt
Glass Melter
Vitrification
Glass Product to Federal Repository
Canyon Air

Figure 10

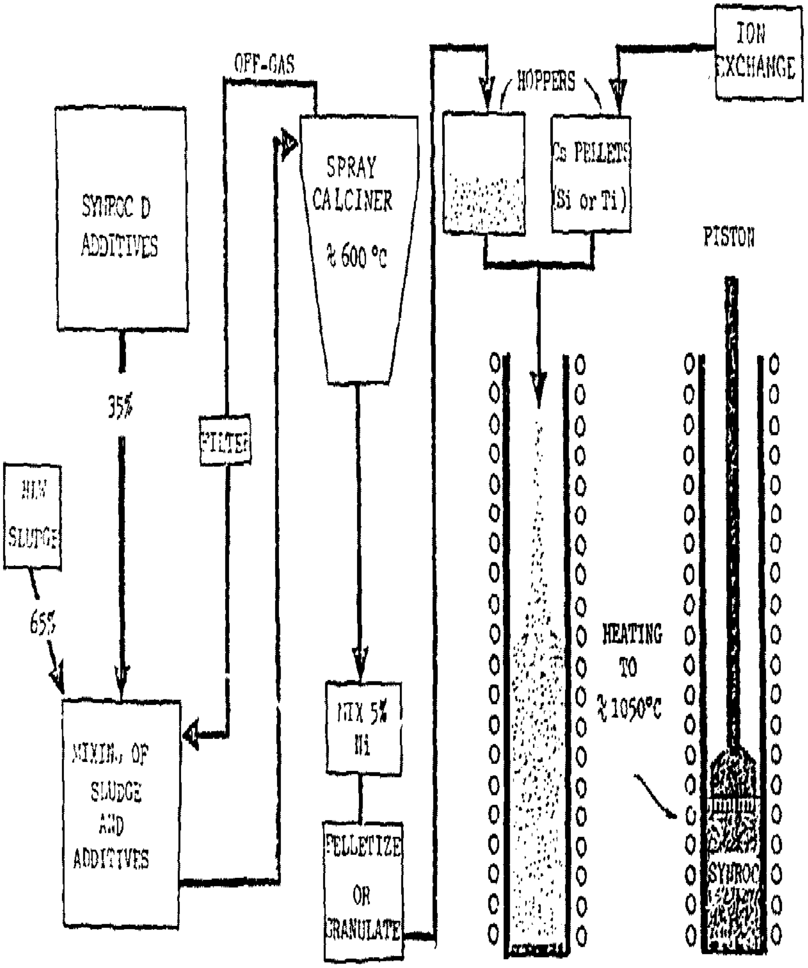
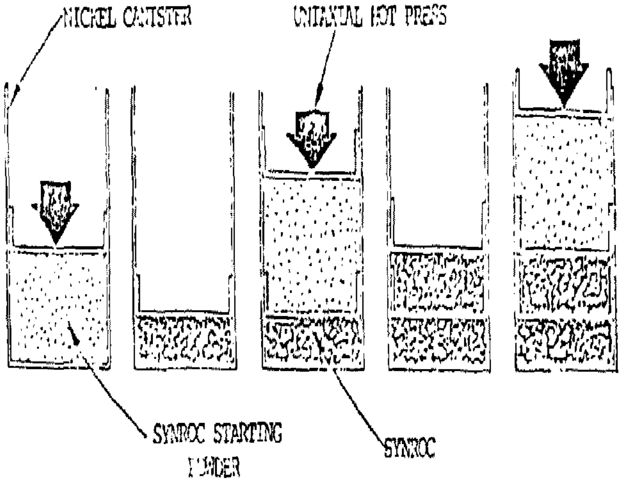

OFF-GAS
SPRAY CALCINER
≈ 600 °C
HOPPERS
ION EXCHANGE
Cs PELLETS (Si or Ti)
SYNROC D ADDITIVES
PISTON
35%
FILTER
HLW SLUDGE
65%
HEATING TO ≈ 1050°C
MIX 5% Ni
MIXING OF SLUDGE AND ADDITIVES
PELLETIZE OR GRANULATE
SYNROC

Figure 11


NICKEL CANISTER
UNIAXIAL HOT PRESS
SYNROC STARTING POWDER
SYNROC

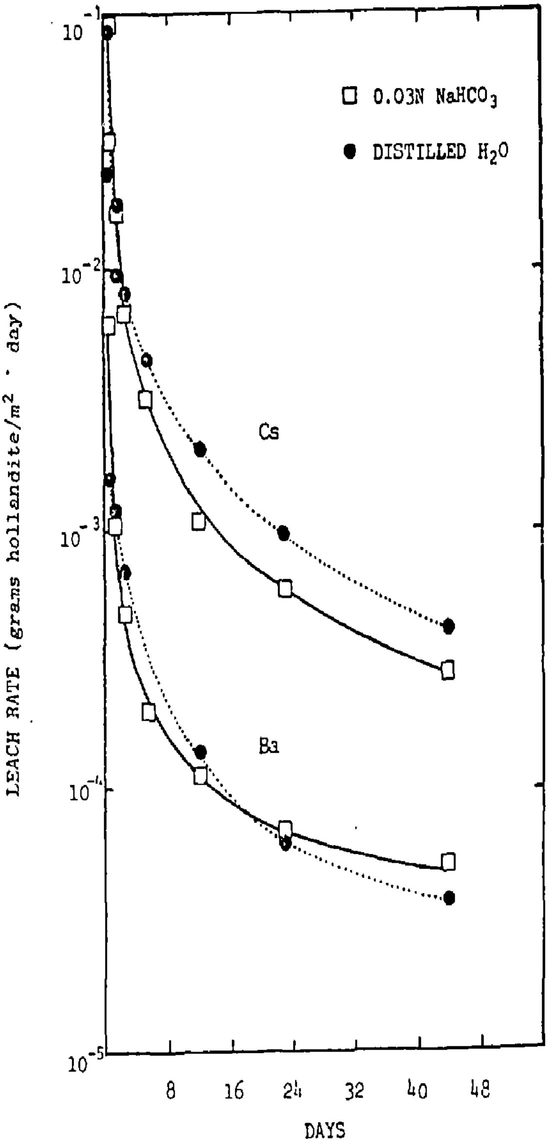

LEACH RATE (grams hollandite/m² · day)
10⁻¹
10⁻²
10⁻³
10⁻⁴
10⁻⁵
0.03N NaHCO₃
DISTILLED H₂O
Cs
Ba
8
16
24
32
40
48
DAYS

Figure 12

Figure 13

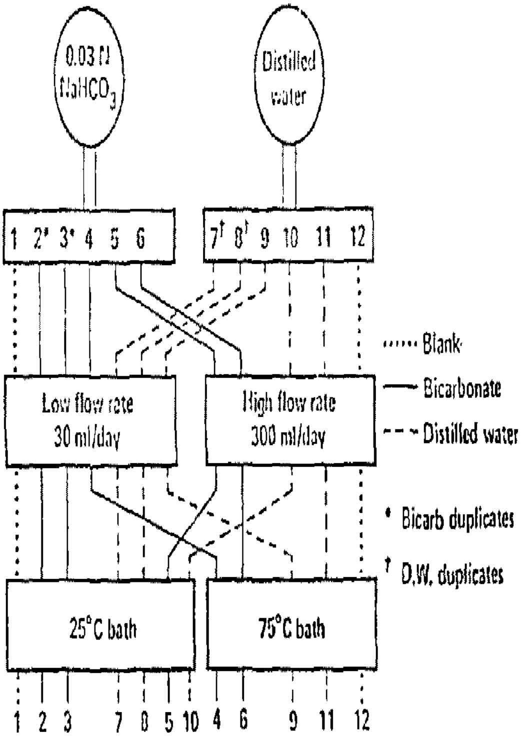

0.03 N NaHCO$_3$
Distilled water
1 2* 3* 4 5 6
7† 8† 9 10 11 12
Low flow rate 30 ml/day
High flow rate 300 ml/day
25°C bath
75°C bath
1 2 3 7 8 5 10 4 6 9 11 12
······ Blank
—— Bicarbonate
- - - Distilled water
* Bicarb duplicates
† D.W. duplicates

Figure 14

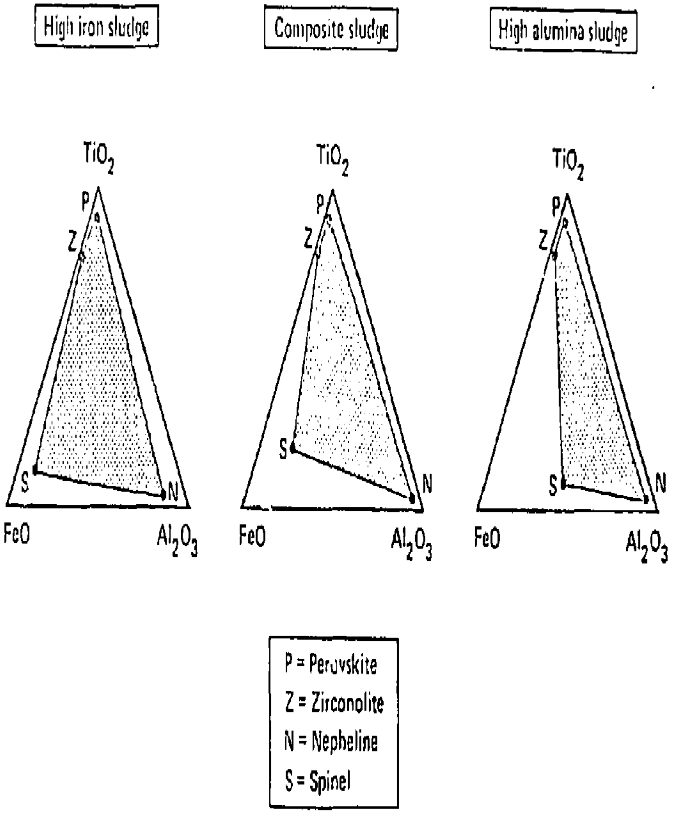

High iron sludge
Composite sludge
High alumina sludge
TiO$_2$
P
Z
S
N
FeO
Al$_2$O$_3$
TiO$_2$
P
Z
S
N
FeO
Al$_2$O$_3$
TiO$_2$
P
Z
S
N
FeO
Al$_2$O$_3$
P = Perovskite
Z = Zirconolite
N = Nepheline
S = Spinel

Figure 15

THE CRYSTAL STRUCTURE OF SYNROC MINERALS