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THE DEVELOPMENT AND TESTING OF SYNROC FOR HIGH LEVEL RADIOACTIVE WASTE FIXATION

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INTRODUCTION

Research and development on the SYNROC concept[1] for high level radioactive waste fixation commenced at the AAEC Research Establishment, Lucas Heights, in March 1979, in collaboration with a complementary program at The Australian National University (ANU). The present paper, taking as its starting point a report[2] on the first year's progress at Lucas Heights which was presented to WASTE MANAGEMENT '80, reports progress in the project's second year and reviews its current status.

SUMMARY OF PROJECT AND FIRST YEAR'S PROGRESS

The SYNROC project at Lucas Heights consists of four main strands, viz.:

(i) SYNROC Fabrication Development, using simulated radioactive waste but taking into account the difficulties inherent in eventual use of high level waste.

(ii) Leach Testing of SYNROC, involving systematic atmospheric pressure and hydrothermal tests.

(iii) Accelerated Radiation Damage Testing of SYNROC, using fast neutron irradiation to simulate actinide decay damage.

(iv) Supporting Research, including SYNROC mineral formation and fabrication studies and measurement of relevant mechanical and thermophysical properties of SYNROC.

At the end of the first year:

(i) Hot pressing in graphite dies was the established laboratory method for the fabrication of 99% dense 'SYNROC B',

(i.e. undoped SYNROC) and simulated radwaste-doped 'SYNROC C' in sizes up to 50 mm diameter. Both cold pressing/sintering and hot isostatic pressing were being considered for further fabrication scaleup.

(ii) Soxhlet and hydrothermal (up to 300°C) leach tests were beginning to show the superiority of SYNROC over borosilicate glass, but no detailed results were reported.

(iii) SYNROC B, perovskite and barium hollandite had been irradiated to a fast neutron fluence of ~ 7×10^{19} neutrons cm^{-2}. All specimens were intact, and the changes in their length and density were reported.

(iv) Mineral phase formation studies and friability tests had commenced.

SYNROC FABRICATION DEVELOPMENT

Laboratory Process

The laboratory process developed at Lucas Heights has been used to prepare all SYNROC C specimens on which leach test results are reported. Briefly, fine powders of TiO_2, Al_2O_3, ZrO_2, $BaCO_3$ and $CaCO_3$ plus 10 weight percent of simulated radwaste (Table I), mainly as nitrates, are ball-milled with zirconia media in alcohol. Sufficient nitric acid to convert the carbonates to nitrates is then added. The slurry is dried, calcined in a stream of dry argon-4% H_2 for 16 hours at 1100°C, then cooled and re-milled. In earlier versions of this process, the calcining atmosphere was either air, air to 800 °C then CO_2-7%CO, or entirely CO_2-7%CO. At the re-milling stage, a fine metal powder is added for additional control of oxygen potential during hot pressing. The initial additive was 0.5% nickel, then 0.5% iron and most recently 1% of titanium has been used.

For hot pressing, an over-size graphite die is used; the SYNROC C powder is contained within a cylindrical capsule of either nickel or iron with a crimped-on lid, and this capsule in turn is surrounded by SYNROC B powder. The usual hot pressing temperature has been 1250°C, but 1150 and 1200°C have also been assessed. The standard hot pressing pressure is 6.9 MPa. Occasionally, the SYNROC C has been hot pressed directly in contact with the graphite die.

TABLE I. Typical SYNROC Compositions

SYNROC B		SYNROC C	
Component	(wt.%)	Component	(wt.%)
TiO_2	59.5	SYNROC B	85
ZrO_2	11.4	Simulated radwaste	10
Al_2O_3	6.0	Additional TiO_2[b]	4
BaO[a]	7.2	Additional Al_2O_3	1
CaO[a]	15.9		

Simulated Radwaste

Component	(wt.%)	Component	(wt.%)
CeO_2	9.7	ZrO_2	14.3
Nd_2O_3	28.3	Cs_2O	8.4
Eu_2O_3	4.4	SrO	6.2
FeO	9.6	NiO	2.8
MoO_2	16.3		
			100.0

a Added as carbonates
b Recently, up to 10% additional TiO_2 has been used

Characterization tests on SYNROC C specimens cut from as-fabricated blocks include bulk density (normally close to 99% of theoretical); open porosity (normally below 0.1%); the presence of the three desired phases — barium hollandite, perovskite and zirconolite — and the absence of reactant or undesired phases (by X-ray diffraction); and the location of critical radwaste elements (by scanning electron microscopy with energy dispersive X-ray analysis — see Table II).

Fabrication Scaleup

The laboratory process was developed quickly to prepare good quality test specimens, and was not intended for further scaleup. At the end of the first year, development of a realistic larger-scale fabrication process became a major aspect of the project, with the laboratory process still being used to prepare test specimens.

In-house funding for fabrication development is being supplemented by grants made under the Australian Government's National Energy

Research, Development and Demonstration Program. It has therefore been possible to design and build at Lucas Heights a 30 kg-scale inactive SYNROC C fabrication line incorporating all necessary stages from initial powder mixing onwards.

TABLE II. Radwaste Element Distribution in Major Phases in Hot Pressed SYNROC

Phase	Radwaste Elements Detected
Barium Hollandite	Cs, Zr, Mo, Ni, (Nd, Sr, Fe)[a]
Perovskite	Nd, Sr, Ce, Mo, Zr, Fe[a]
Zirconolite	Nd, Sr, Fe[a]

a Observed at low levels

Choice of fabrication method between die hot pressing, hot isostatic pressing or cold pressing and sintering was the key decision to be made. *Cold pressing and sintering* was rejected because the higher temperatures needed for densification and the lack of confinement inherent in the process made the retention of caesium and other volatile radwaste species very difficult. *Hot isostatic pressing* was rejected for development at Lucas Heights, partly because of its high operating pressures and consequent queries on safety under fully active conditions, and partly because a simpler, low pressure method has become available. *Graphite die hot pressing* suffers from the problems of the relatively few pressings which can be obtained from the one die, the significant die costs involved and, under fully active remote operation conditions, the consequent generation of large volumes of contaminated graphite for disposal. The alternative method being developed at Lucas Heights retains the advantages of die hot pressing but avoids the use of graphite.

The new method, known as *in-can hot pressing*, is the subject of joint AAEC-ANU patenting action[3]. Following successful laboratory experiments, it is now the key fabrication step in the demonstration line.

In in-can hot pressing, a closed-end, laterally supported stainless steel tube serves as both the hot pressing die and, after welding-on of a top end cap, a SYNROC disposal canister. The Lucas Heights unit is designed for the repetitive production of high density, fully canned SYNROC blocks of 100 mm diameter and up to 900 mm long. It is confidently predicted that considerable scaleup of this method will be feasible, and that the operating characteristics of the

demonstration unit will allow the design of equipment to produce blocks of at least twice this diameter and the applicable fabrication cycle times to be predicted.

The overall objective of the demonstration line (Fig. 1) is to show that SYNROC fabrication need *not* be particularly complicated or expensive compared with the corresponding methods for borosilicate waste glass fabrication. Carefully chosen powder mixing, simulated radwaste addition, denitration, granulation and calcination steps are therefore included in the line. The very fine initial SYNROC powder components are wet milled in an *attritor* and a simulated radwaste nitrate stream is then added in a *mixing tank*. The slurry is then sprayed into a 100 mm diameter *fluidized bed reactor* where it is dried and partially denitrated. It is expected that the product will be free-flowing homogeneous granules. Spray drying and spray calcination are also being considered as alternatives for this step. Further calcination of SYNROC granules to commence the formation of the SYNROC mineral phases prior to hot pressing is to be carried out in a specially designed *rotary calcining furnace*, in which the inclined rotating stainless steel tube has an internal diameter of 100 mm and a length of 1800 mm. The furnace is designed for operation with a controlled reducing atmosphere, which is currently envisaged to be argon-4% hydrogen. The resultant free-flowing granular calcine will be fed to the *in-can hot press* in thin walled metal cans in stages involving top ram retraction during the hot pressing cycle. The hot pressing temperature is envisaged to be in the range 1200-1250°C. Upon completion of the pressing cycle, the canister containing the required length of densified SYNROC is ejected from the furnace using the lower ram, and sealed by welding-on a top lid or end-cap.

The demonstration line, including the in-can hot pressing stage, is expected to be in operation by mid-1981.

Leach Testing

The leach rate of SYNROC containing 10 weight percent simulated radwaste (Table I) has been determined over the range 45-300°C. Parallel leach tests were undertaken on a borosilicate glass containing the same simulated radwaste composition. For these tests, a borosilicate frit was prepared with the same composition as the PNL glass 73-1[4]. Other borosilicate glasses were kindly supplied by laboratories in USA, Britain and France. To date, about five hundred leach tests have been carried out for the routine evaluation of developmental SYNROC pressings and to compare systematically the leach resistance of well-formed SYNROC and borosilicate glasses.

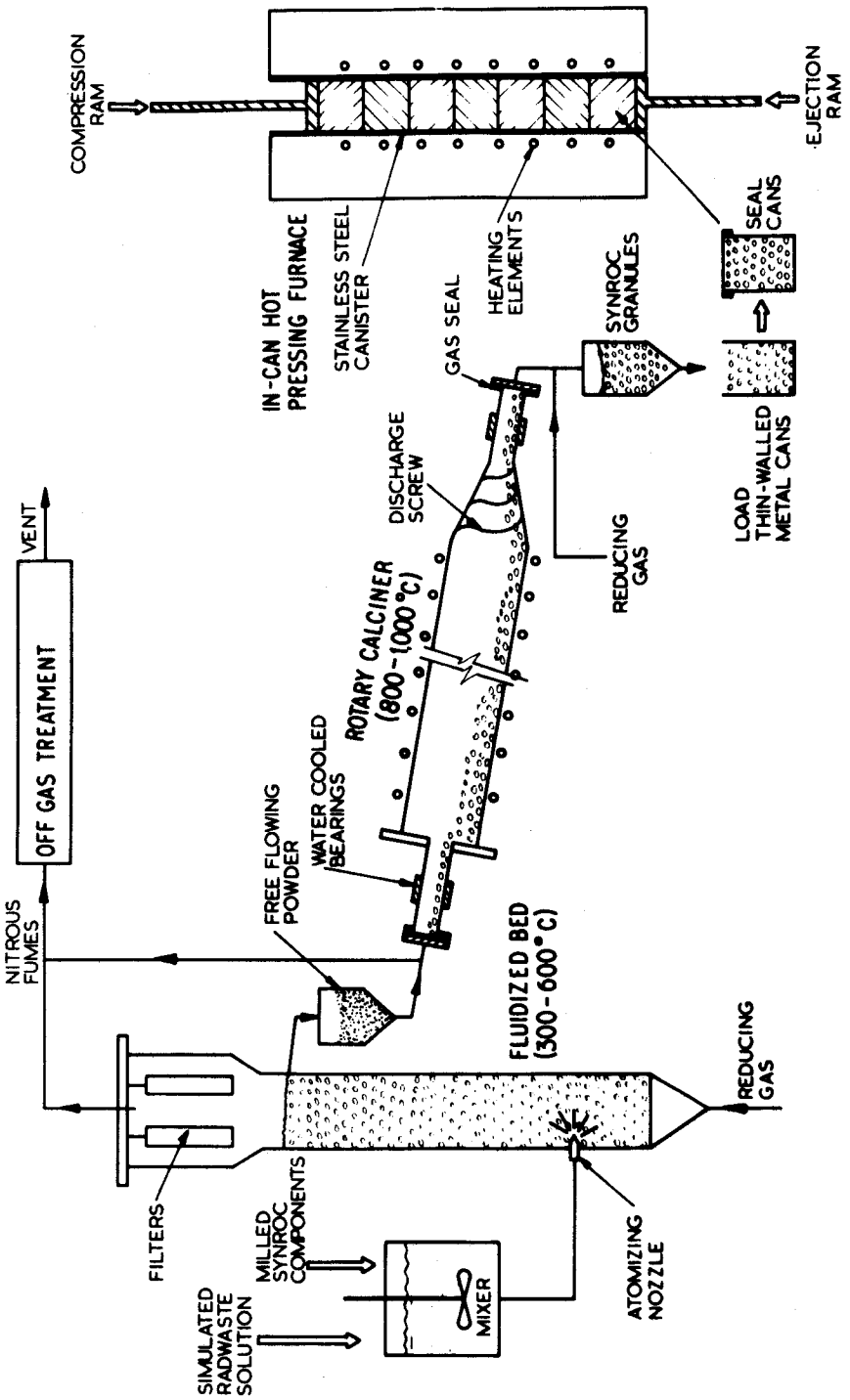

FIGURE 1. SCHEMATIC LAYOUT OF SYNROC FABRICATION LINE AT LUCAS HEIGHTS

The procedures used in leach tests were in general accordance with the method[5] issued by the International Organisation for Standardisation (ISO). This test, which is based on the recommendations of the IAEA[6], involves regular replenishment of leachant to simulate groundwater circulation. It therefore minimizes solution saturation effects which can give misleadingly low leach rates in long-term static tests. The ISO procedure was modified to the extent that the water was always replaced daily rather than with the decreasing frequency recommended in the test. This was done to avoid saturation effects, which might dominate as the replacement frequency was reduced and be misconstrued as a decrease in the intrinsic leach rate.

In the absence of an internationally approved hydrothermal test, the ISO procedure was followed for experiments above 100°C with the appropriate minor modifications required for autoclave experiments. Hydrothermal tests were carried out in 25 mL Teflon-lined stainless steel or Monel vessels. A number of these vessels were placed in either a heated aluminium block or a one litre electrically heated autoclave containing water.

Most leach tests were conducted on discs, 10 mm diameter x 2 mm thick. In some experiments, the leach rate using discs of SYNROC was so low that key waste elements could not be detected in the leachant. The sample was then crushed, sieved and the 100-150 mesh fraction used. The leach rate was based on the geometric surface area as calculated from published data on crushed minerals[7]. For 100-150 mesh SYNROC powder, the geometric surface area was estimated to be 1.9 times the surface area of a sphere of the same sieve size.

Disc specimens were weighed to determine the overall leach rate, while the solutions were routinely analyzed for caesium, strontium and europium (representing rare earths) by atomic absorption spectroscopy. On occasions the solutions were also analyzed for other key elements (e.g. Ti, Si, U, Mo, Ca, Al, Fe). To increase the sensitivity for some elements, particularly caesium, the neutron activation analysis method developed by Flynn et al.[8] was also used.

Initial leach tests were broad in scope and intended to determine the best conditions for making SYNROC. Powder homogeneity, calcination conditions, oxidation potential and hot pressing temperature were shown to be important. Caesium leachability was progressively reduced when the calcination atmosphere was changed from air to CO_2-7% CO and finally to the more reducing Ar-4% H_2. It is believed that the more reducing atmospheres prevent the formation of soluble caesium molybdate. The substitution of metallic iron for nickel to control the oxygen potential during hot pressing also improved the leach resistance. The effect of titanium additions is now being studied.

Leaching tests were carried out on SYNROC hot pressed at 1150°C, 1200°C and 1250°C. SYNROC formed at 1200°C was marginally superior to that formed at 1250°C. The SYNROC block formed at 1150°C was slightly porous at the hot pressing pressure of 6.9 MPa used in these experiments. This allowed water to penetrate the sample thereby increasing the surface area exposed to leachant. Consequently, SYNROC pressed at 1150°C had the highest leach rate.

Initial tests showed that caesium and strontium were the most leachable radwastes in SYNROC and, subsequently, attention was focused on these elements. Figure 2 shows the effect of temperature on the initial leach rate of SYNROC and borosilicate glass. Well-formed SYNROC was superior to glass over the entire temperature range. Compared to glass, the leach rate of SYNROC does not increase greatly with temperature. This is illustrated by the fact that the overall leach rate of SYNROC increased by a factor of 25 over the temperature range 45-300°C whereas the rate for glass increased by a factor of 250. Overall leach rates for the borosilicate glass used in this work are similar to those published for PNL glass 76-68[9].

The leach rates for caesium and strontium from SYNROC are significantly above the overall rate and conform to the Arrhenius relationship (Fig. 2). Activation energies based on mass, caesium and strontium loss are 19.4, 25.7 and 14.6 kJ mol^{-1} respectively. Although the leach data for glass are also shown on the Arrhenius plot, close examination suggests a more complex relationship. The results for strontium which show a maximum leach rate at 200°C are particularly anomalous. Above 200°C, the leachant becomes quite alkaline (pH > 9 measured after cooling to 45°C) and strontium is probably removed from solution by precipitation and/or adsorption processes.

The elements comprising the SYNROC matrix (Al, Ba, Ca, Ti, Zr) were very resistant to leaching. The leach rate based on these elements was generally below the overall rate based on mass loss. Titanium was never detected in solution even after hydrothermal attack at 300°C. Calcium was the most leachable matrix element; its leach rate at 100°C was below that of strontium and approximately the same as the overall leach rate.

Limited experimental data indicate that rare earths and actinides are retained within SYNROC; at 100°C the initial leach rate for europium was below the detection limit of 0.005 g m^{-2} day^{-1}. Uranium was added to waste in a few experiments to simulate actinides. The leach rate from well-formed SYNROC at 300°C was below the detection limit of 0.1 g m^{-2} day^{-1}.

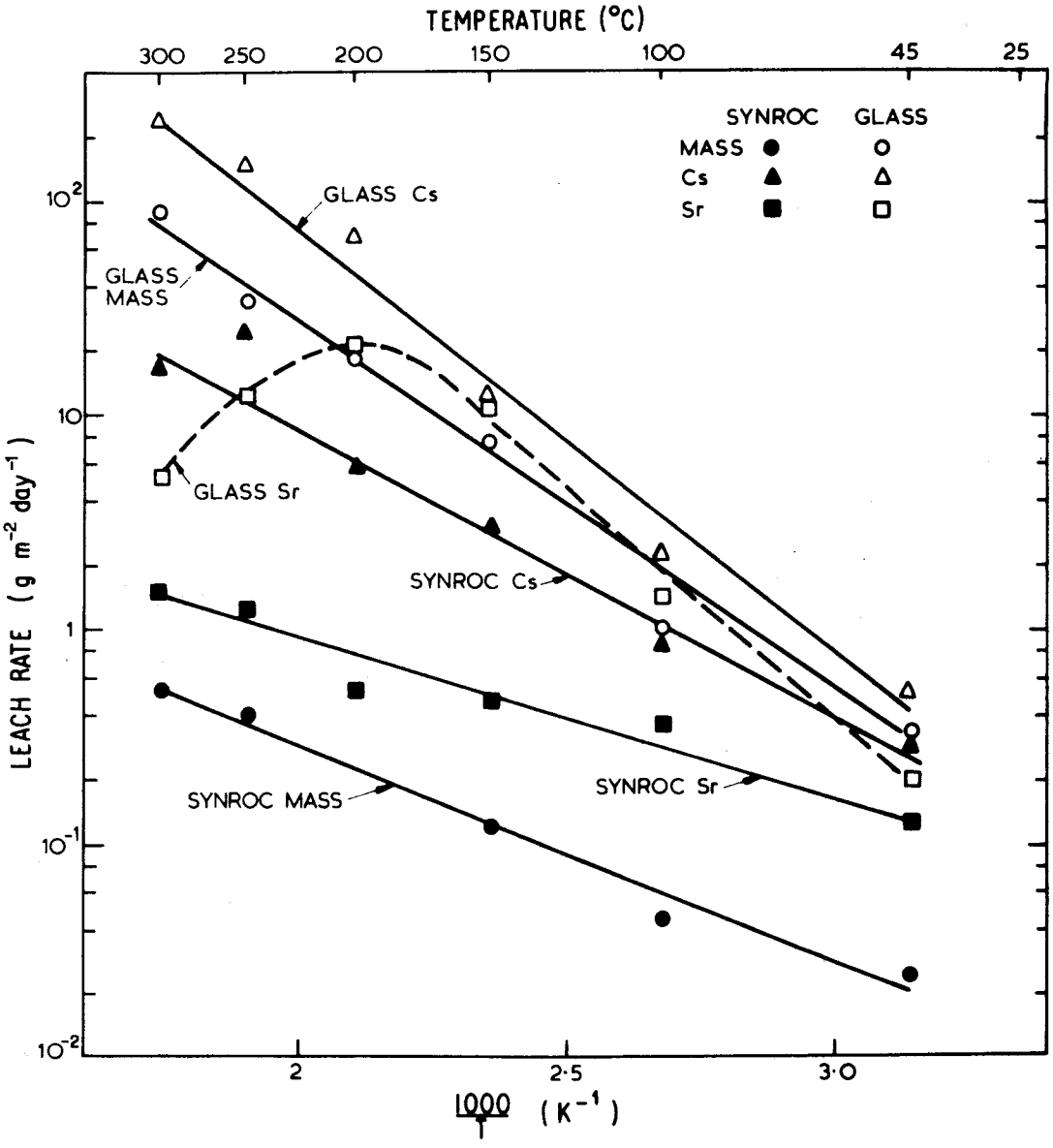

Figure 2 Effect of temperature on initial leach rate of SYNROC and borosilicate glass (PNL 73-1) containing 10 weight % simulated radwaste.

(Leachant: deionized water. Leaching time: 1 day. Leachant volume/sample surface area = 0.1 m).

Figure 3 shows the effect of time on the accumulated quantities of caesium and strontium leached from SYNROC and two borosilicate glasses by deionized water at 100°C. Tests were carried out on both SYNROC discs and 100-150 mesh powders. The tests with powders were

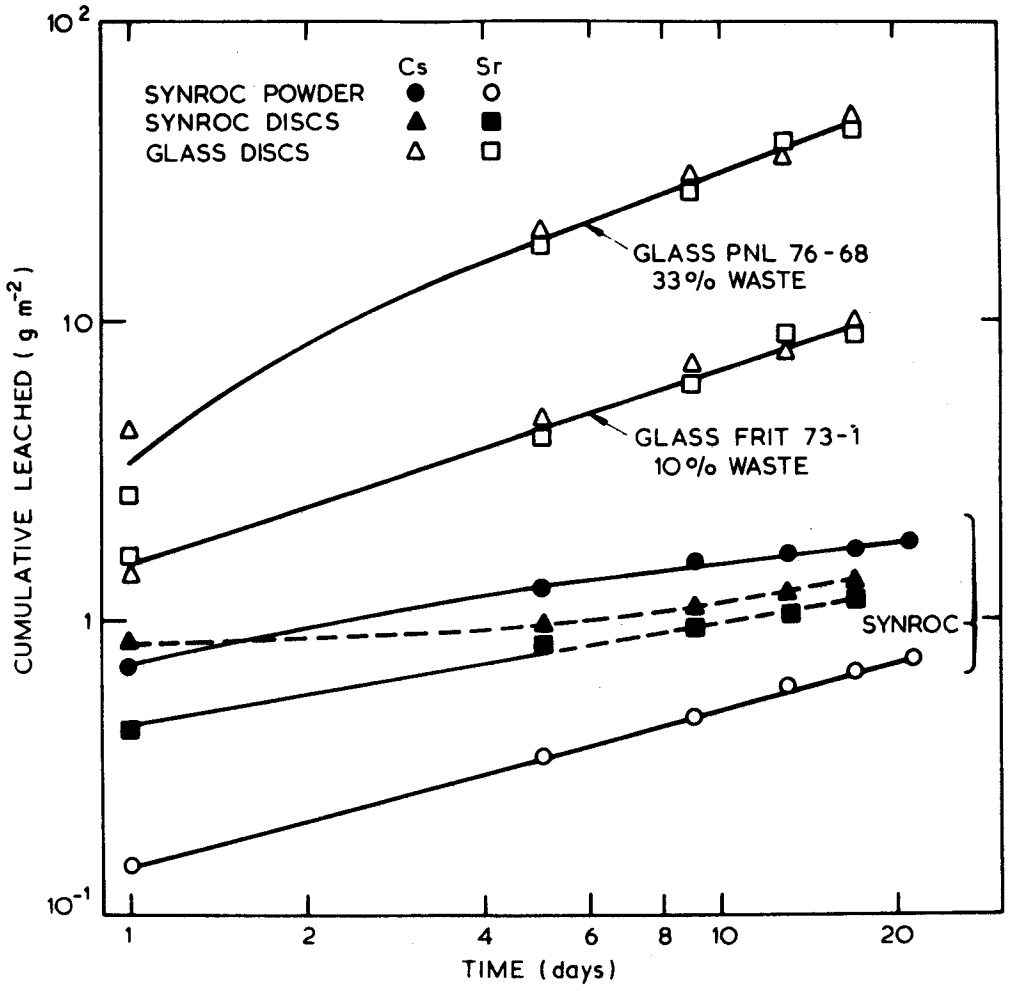

Figure 3 Cumulative quantities of caesium and strontium leached from SYNROC and borosilicate glasses.

(Leachant: Deionized water replaced daily. Temperature: 100°C. For discs: Leachant volume/area = 0.1 m. For 100-150 mesh powders: Leachant volume/geometric surface area = 0.0017 m).

begun when experiments with discs had shown that both caesium and strontium were undetectable after the fifth day of leaching. The dotted lines in Fig. 3 therefore represent upper values for discs corresponding to the lower detection limits. Considering the uncertainties in estimating geometric surface area, the agreement between experiments with discs and powders is reasonable.

The leach rate of caesium and strontium from SYNROC decreased markedly with time. Initial leach rates based on powder experiments were 0.72 g m^{-2} day^{-1} for caesium and 0.15 g m^{-2} day^{-1} for strontium. After nineteen days, the leach rate had dropped to 0.019 g m^{-2} day^{-1} for caesium and 0.016 g m^{-2} day^{-1} for strontium.

The cumulative leach data for caesium and strontium from borosilicate glasses can be represented by a single curve. The quantities of these elements leached from borosilicate glasses are considerably greater than for SYNROC. Moreover, the superiority of SYNROC becomes more apparent with increasing time because the leach rate for glasses does not decrease to the same extent as for SYNROC.

Long-term leach results for glasses are often represented by an equation of the form[10]

$$Q \text{ (amount leached)} = a\sqrt{t} + b\,t \qquad (1)$$

where the first term on the right hand side represents diffusion through a surface layer and the second term represents uniform or 'congruent' dissolution. The data in Fig. 3 conform to this equation with the slope of log Q versus log t being intermediate between 0.5 and 1. On the other hand, the slopes of the curves for SYNROC are ≤ 0.5, suggesting a diffusion mechanism.

Comparatively few leach results have been reported for SYNROC[11-14]. Most of the data are confined to caesium and cover the temperature range 75-85°C. Coles and Bazan[11] carried out dynamic leach tests on SYNROC cores and powders at 75°C. Their leach rates, when recalculated on the basis of geometric surface area, are somewhat higher than the results reported here, but those of Ringwood et al.[12] and Solomah and Zumwalt[13] are very similar. In this study, the leach rate of caesium after seven days was 0.05 g m^{-2} day^{-1} at 100°C which compares with a value of 0.08 g m^{-2} day^{-1} reported by both Ringwood et al. at 85°C and Solomah and Zumwalt at 75°C. These authors also found that the leach rate decreased markedly with time; for example, Ringwood reported 0.007 g m^{-2} day^{-1} after 25 days and Solomah 0.002 g m^{-2} day^{-1} after 43 days.

Although SYNROC as currently produced is obviously very resistant to groundwater attack, there is scope for further improvements in fabrication technology. We are continuing to refine fabrication methods with the aim of producing an even more leach-resistant material.

ACCELERATED RADIATION DAMAGE TESTING

Fast neutron irradiation is being used to produce displacement damage in SYNROC B, SYNROC C and the separate SYNROC minerals as a means of simulating long term actinide decay damage in SYNROC containing radioactive waste. Some results from the first (1979) irradiation experiment were presented[2] at WASTE MANAGEMENT '80. More recently, this work was reported in more detail[15] and a second series of irradiations is beginning to produce results.

In the 1979 experiment, SYNROC B, perovskite and barium hollandite, all prepared by cold pressing and sintering in air, were irradiated in a pile temperature rig in the AAEC's materials testing reactor HIFAR for one operational period (22 days) to an integrated fast neutron (> 1 MeV) flux of 6.5×10^{19} neutrons cm^{-2}. Displacement damage calculations gave a displacements per atom (dpa) value of 0.18. When compared with the calculated dpa's from alpha particle emission and actinide recoil effects in fully active SYNROC C, this suggested a SYNROC age of 10^4 years. However, because the barium hollandite phase should contain no actinides and will therefore be subject only to α-particle damage, the fast neutron experiment in fact simulated a hollandite age of at least 10^6 years.

All specimens were intact after irradiation, but the perovskite, and to a lesser extent the barium hollandite, showed some chipping and cracking. Metallographic examination showed microcracking in these two materials but there was little microcracking, and no macrocracking, in the SYNROC. Linear expansions were measured on all materials.

In a second, much larger program, SYNROC B, SYNROC C, barium hollandite, perovskite and zirconolite specimens are being irradiated for 1, 2, 4 and 6 reactor periods, simulating ages of ~ 10^4, ~ 10^5, ~ 5×10^5 and ~ 8×10^5 years respectively (except for barium hollandite, see Table III). All specimens were made under reducing conditions, either by hot pressing in graphite or by sintering in CO_2-7% CO. Some volume expansion results from this program and the first irradiation experiments are presented in Table III. Three of the 4 two-period perovskite specimens split cleanly across a diameter during or after irradiation, otherwise all specimens were intact. Detailed microscopic examination is in progress.

TABLE III Summary of Fast Neutron Irradiation Results on SYNROC and SYNROC Minerals

Reactor Period Number[a]	Simulated Age (y)	Per Cent Volume Expansion[b]				
		Hollandite	Perovskite	Zirconolite	SYNROC B	SYNROC C
271	9×10^3	-	-	1.7	1.4	1.7-2.2
254	10^4	-	2.6[c]	-	1.7[c]	-
266	1.7×10^4	-	2.2	-	3.5	-
267/268	10^5	-	3.4	-	5.5	-
254	$> 10^6$	1.4[c]	-	-	-	-
266	$> 10^6$	0.9	-	-	-	-
267/268	$> 10^7$	1.9	-	-	-	-

a The fast neutron flux differed significantly between reactor periods
b Mean of 3 or 4 specimens in each case
c 1979 irradiation experiment; volume expansions inferred from length changes.

More results are needed before definite conclusions can be drawn from this work. However, at this stage we can say that:

(i) For the same fast neutron dose, the volume expansion appears to increase in the order barium hollandite < perovskite < SYNROC B, with zirconolite and SYNROC C, from results at one dose only, expanding marginally more.

(ii) The four points for SYNROC B, when plotted against either fast neutron dose or log (simulated age), fall on a smooth S-shaped curve, suggesting a saturation value of volume expansion of about 6.5%.

SUPPORTING RESEARCH

Mineral Formation and Fabrication Studies

The first phase of this work[16], which was based on one particular set of TiO_2, ZrO_2, Al_2O_3, $BaCO_3$ and $CaCO_3$ powders, involved no simulated radwaste additions and used cold pressing and air sintering.

Traditional ceramic methods were used to prepare powders for the fabrication of specimens of > 97% theoretical density and < 0.1% open porosity of the three-phase ceramic SYNROC-B and its constituent mineral phases. The optimum sintering temperatures were 1310°C for perovskite and SYNROC-B, 1400°C for zirconolite and 1270°C for barium hollandite.

The synthesis of zirconolite involved perovskite as an intermediate phase whereas that of barium hollandite proceeded via two intermediate phases, $BaTiO_3$ and $BaTi_4O_9$. The synthesis of SYNROC-B also proceeded via these intermediate phases. At one stage of the synthesis, perovskite was present in excess of the amount in the final product. Conversion of the excess perovskite to zirconolite was slower than the formation of barium hollandite.

Fully synthesized, fine, sinterable powders of perovskite, zirconolite and SYNROC-B could be produced by calcining compacts for 16 h at 1100°C, 1300°C and 1200°C respectively. However, complete synthesis of the barium hollandite required a calcination temperature of 1200°C, whereas, to obtain a fine powder, the maximum allowable temperature was approximately 1000°C. The preparation of a sinterable, but partially reacted, barium hollandite powder required two calcination stages of 24 h, each at 1050°C.

Because the high calcination and sintering temperatures could lead to a loss of volatile elements, the methods used in this study are not considered suitable for the fabrication of radwaste-doped SYNROC C. A second phase of this work, now in progress, involves simulated radwaste additions, finer powders, sintering in reducing atmospheres at lower temperatures and hot pressing in graphite dies.

Impact Friability Testing

Various SYNROC B and SYNROC C specimens have been subjected to a friability test[17] involving 217 J impacts and particle size analysis of the resultant powder. Material variables included in the study were cold pressing and sintering (both in air and CO/CO_2) v. hot pressing, presence or absence of simulated waste and grain size of the sintered SYNROC. This last variable applied to SYNROC B only, sintered and annealed in air for various times up to 500 h. The grain size range covered was 4 to 34 μm.

The results[18] showed that impact friability in this test was relatively insensitive to the material variables studied. However, there were minor differences in the extent of fine particle production in the important size fraction below 10 μm, where hot-pressed SYNROC B and C produced fewer fines than cold pressed and sintered materials (Table IV). SYNROC also produced a marginally coarser powder over the whole size range studied (2-100 μm) compared with the results reported[17] for the US borosilicate waste glass ICM-11 [PW-7-2(2.0)73-11]. A similar base glass prepared at Lucas Heights also gave finer powder above 50 μm (the lower limit of particle size analysis in this one case) than SYNROC.

TABLE IV Extent of Fine Fractions in Impact Friability Test (all in wt.%)

Size Range (μm)	Air Sintered SYNROC B	CO/CO_2 Sintered SYNROC B	CO_2/CO_2 Sintered SYNROC C	Hot Pressed SYNROC B	Hot Pressed SYNROC C	Waste Glass ICM-11
< 20	4.0	4.0	4.0	1.3	4.0	5.0
< 10	2.0	2.0	2.0	1.0	1.1	2.5
< 5	0.8	0.8	0.9	0.4	1.0	1.0

Thermal Diffusivity/Conductivity and Specific Heat

These properties are being measured between 25° and 700°C for SYNROC B, SYNROC C, perovskite, zirconolite and barium hollandite by the laser flash method. Initial results for SYNROC B (density 4.27 g cm^{-3}) are shown in Fig. 4. Generally, the thermal diffusivity of SYNROC B is about three times higher than that of a typical borosilicate glass (Corning 7740[19]); the specific heat is up to 20% below that of a similar glass[20]; and the thermal conductivity is about four times higher than that of either Pyrex 7740[21] or the PNL waste glass 72-68[4].

CONCLUSION

Progress in SYNROC research and development at Lucas Heights has been made on a broad front. An inactive 30 kg-scale SYNROC fabrication line incorporating *in-can hot pressing* as the fabrication step has been built for operation in mid 1981. Atmospheric pressure and hydrothermal leach tests are demonstrating the excellent leach resistance of SYNROC. Accelerated radiation damage tests using fast neutrons are simulating damage in SYNROC for periods of close to 10^6 years. In supporting research, mineral phase development, impact friability and thermophysical properties of SYNROC are being studied.

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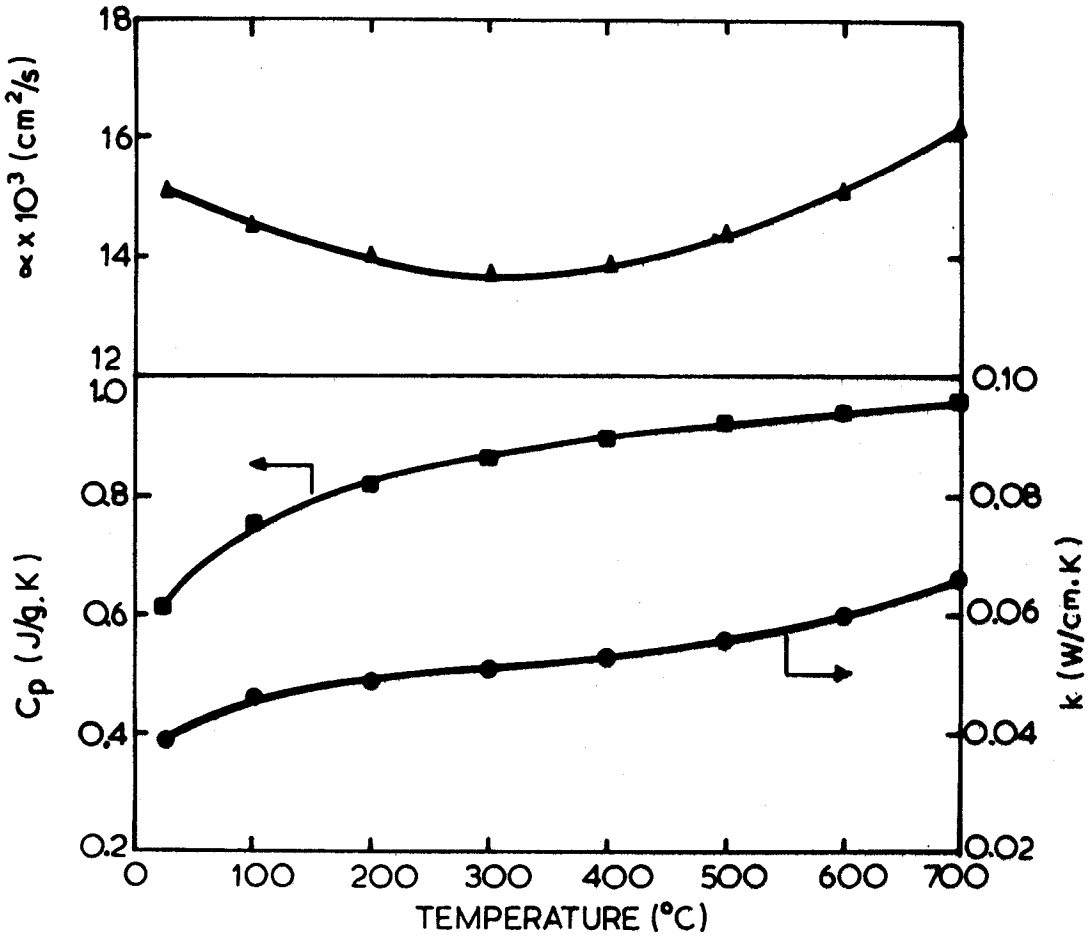

Figure 4 Thermal diffusivity, α, specific heat, C_p, and thermal conductivity, k, of SYNROC B.

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