Second United Nations
International Conference
on the Peaceful Uses
of Atomic Energy

A/CONF.15/P/46
UNITED KINGDOM
6 June 1958

ORIGINAL : ENGLISH

SOME CHEMICAL PROBLEMS OF HOMOGENEOUS AQUEOUS REACTORS

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1. Homogeneous aqueous reactor (H.A.R.) systems have been the subject of a feasibility study at A.E.R.E., Harwell, since 1954. This paper presents the results of our investigations on some of the more important of the chemical and chemical engineering problems involved. Much of the feasibility study has been devoted to a two-zone H.A.R. based on a uranyl sulphate solution core of the same type as that developed at Oak Ridge, U.S.A. The chemical studies have ranged more widely through the possible H.A.R. systems, however, and we will discuss primarily those aspects which differ from the Oak Ridge design.

2. A description of the various types of H.A.R. has appeared in a recent publication(1) and it is considered unnecessary to include a general discussion of them here.

1. AQUEOUS SOLUTION STUDIES

1.1 The Corrosion Problem of the Two-Zone System

3. The major factor which is holding back the rapid development of a two-zone H.A.R. system (which has nuclear advantages over a single-zone system) is the requirement for a neutron "window" vessel between the fissile core and the fertile blanket. This vessel must be transparent to neutrons, have reasonable mechanical strength to withstand pressure transients, and have good corrosion resistance to the working fluids.

4. Since aluminium has neither good mechanical strength nor sufficient corrosion resistance to aqueous solutions at 300°C., and since little is

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(1) Wells, I., and Newby, D. The homogeneous aqueous reactor, Nuclear Engineering, 2: 146-151, 2: 275-285 (1957).

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*U.K. Atomic Energy Authority, A.E.R.E., Harwell.

known of low neutron cross section beryllium, the choice for the window material is restricted to hafnium-free zirconium alloys. Titanium and niobium may also be considered, but their neutron cross sections are too high for use of these metals throughout the core vessel - they could perhaps be used as linings to a zirconium vessel if they were found to have superior corrosion resistance.

5. The core vessel would be subject to corrosion at temperatures up to 300°C. by an aqueous fissile solution on the inside and an aqueous fertile slurry on the outside. Discussion of the corrosion problem below is restricted to the core fluid.

6. A solution core for an H.A.R. might consist of uranyl fluoride, nitrate, carbonate or sulphate. Under suitable pH conditions each of these compounds would have ample solubility for use in the reactor; all other compounds may be eliminated on grounds of neutron economy. Since it is necessary to base the construction of the core vessel on zirconium, we may neglect the use of uranyl fluoride: excess hydrofluoric acid necessary to prevent hydrolysis would have a serious effect upon corrosion.

7. Zirconium relies for its corrosion resistance upon a protective oxide film. The rate at which the metal is transformed into oxide by the out-of-pile corrosion reaction is dependent upon diffusion processes taking place within the oxide(2). Unless the diffusion constants of the oxide can be modified by the inclusion of ions from the solution, the solution composition would be expected to have a negligible effect upon the corrosion rate. This expectation is confirmed by the results available. For instance, corrosion experiments at A.E.R.E. have shown that the out-of-pile corrosion behaviour of zircaloy-2 in standard test solution is identical with that reported by Thomas(2) for corrosion by pure water. The standard test solution is defined as: 0.04 M. uranyl sulphate, 0.02 M. sulphuric acid and 0.005 M. cupric sulphate. Thomas also listed a considerable number of additives whose presence in the water had no detectable effect on the corrosion process.

8. Experiments at Oak Ridge have shown that zirconium and its alloys corrode linearly with time under irradiation and the corrosion rate is dependent upon the fission power density(3). Again, solution composition appears to be a relatively unimportant variable. It appears reasonable to discuss the problem of the core vessel corrosion in general terms, therefore, without relating it to any specific choice of core fluid.

9. The design study(1) of a 100 MW(E) two-zone breeder reactor at A.E.R.E. has required a neutron window vessel $\frac{5}{8}$" thick. This dimension is a delicate balance between several opposing factors. If the vessel is appreciably thinner then this places severe restrictions on the device for pressure

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(2) Thomas, D.E. Metallurgy of zirconium. McGaw-Hill Co. Inc., National Nuclear Energy Series, VII - 4: 635 (1955).

(3) Jenks, G.H. H.R.P. Civilian Power Reactor Conference. U.S.A.E.C. Report TID-7540: 232-240 (1957).

balancing between core and blanket circuits, and if the vessel is thicker the position is soon reached where excessive neutron losses occur by capture in the zirconium and thermal stresses become unacceptable. Very little loss of thickness by corrosion could be tolerated, and a corrosion rate of 1-2 mil/year represents about the upper limit which is acceptable assuming that the vessel must remain in the reactor for 20 years.

10. The proposed design is based upon a minimum power density at the vessel wall of 15-17 kW/litre. The Oak Ridge data on zircaloy-2 suggest that a penetration rate of ~ 25 mil/year would be obtained at this power density: a factor of 10-20 greater than acceptable.

11. Since the corrosion rate is dependent upon the power density in the solution, it is interesting to note the relative rates of energy deposition in the protective oxide film on a metal under irradiation. The oxide film will be subject to bombardment by several different types of radiation and it is important to decide which radiation is responsible for the marked effect upon corrosion. In the reference design of reactor, calculation showed that the total energy deposition in a zirconium dioxide film one micron thick would be sub-divided approximately thus:

Fast neutrons	< 1%
Beta decay energy	18
Instantaneous gamma energy	69
Fission recoil fragments	12

Present evidence indicates that there is little effect on the corrosion rate from either beta or gamma radiation(4). Fast neutrons might be as effective as the fission recoil particles at equal energy deposition rates, but fortunately the fast neutron flux is sufficiently low for this effect to be neglected.

12. It appears, therefore, that total energy deposition rates in the protective oxide film are not directly related to increases in corrosion rate under irradiation. Rather it is the increased number of displaced atoms and vacancies in the oxide lattice which should be considered. This conforms much more closely with the experimental evidence that beta and gamma fluxes are the least damaging radiations present in the reactor. In the absence of any secondary effect, the result of irradiation of the oxide film with fission fragments or fast neutrons will be an increase in the diffusion constants of the oxide film, leading to an increased corrosion rate. It can be shown, however, that as a result of annealing effects and the high mobility of the defects produced, a stationary state is likely to be reached where the diffusion coefficients are again constant although higher than in the unirradiated oxide. We would then expect the corrosion rate to be approximately linear initially, and greater than for unirradiated samples,

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(4) Heston, B.O. and Silverman, M.D. Effects of electron irradiation on the corrosion of zircaloy-2. U.S.A.E.C. Report, ORNL-CF-56-2-2.

but to return gradually to an approximately $\frac{1}{3}$-order rate law as in out-of-pile experiments. In-pile corrosion investigations do not support this, however; the corrosion rate remains a linear function of time(3).

13. It is necessary, therefore, to consider secondary effects which could account for the linear time dependence. Following reports(5,6) that transformation of zirconium dioxide from the monoclinic form to the cubic form could be accomplished by fast neutron irradiation with $1\text{-}2\times10^{20}$ nvt, it was suggested that a similar transformation occurring in contact with fissioning uranium solution could result in mechanical failure of the oxide film. Normally the cubic structure is stable only at very high temperatures. We have studied the effect of energy deposition from fission fragment bombardment on the structure of metallic oxide films. The technique used has been to place the oxide film in close proximity to a foil coated with a very thin layer of U_3O_8. By performing the irradiation in air, rather than in aqueous solution, a high proportion of the fission fragment energy can be absorbed in the zirconium oxide film. In fact the attainable rate of energy deposition from irradiations of this kind in BEPO is greater than that expected from the uranyl sulphate solution in the power reactor. An example of the results is shown in Figure 1. The oxide film (~8 microns thick) was formed on samples of a 5% vanadium alloy of zirconium by out-of-pile exposure to 0.04 M. Na_2SO_4/0.02 M. H_2SO_4 solution at 300°C. The film was originally monoclinic and the Figure shows the amount transformed to the cubic modification as a function of the integrated fission fragment flux. The transformation was determined by a glancing-angle X-ray diffraction technique. Evidently an integrated fission fragment flux of approximately 7.5×10^{14} per cm^2 is required to produce 90% transformation. This is equivalent to an irradiation time of approximately 100 days in uranyl sulphate solution at 5 kW/litre power density. The amount transformed after the equivalent of one day under the same conditions is ~4% and unless such a small amount of transformation could be shown to result in mechanical failure of the oxide film this mechanism for the corrosion enhancement by irradiation must be discounted.

14. A further mechanism for the enhanced irradiation corrosion lies in the possibility of a higher solution rate of the protective oxide film. Out-of-pile, the solution rate of zirconium dioxide in the type of solution we are considering is negligible and there is no direct experimental evidence that the rate is increased under irradiation. Until further evidence is available, however, this would seem to be the most probable explanation of the effect. Increased solubilities following irradiation have been observed in other systems(7,8).

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(5) Johnson, J.R. Development of a cubic oxide protective film on zirconium. U.S.A.E.C. Report, ORNL-2029.

(6) Wittels, M.C. and Sherrill, F.A. Irradiation induced phase transformation in zirconia. J. Appl. Phys. 27: 643 (1956).

(7) Simnad, M. and Smoluchowski, R. The effect of proton irradiation on the rate of solution of Fe_2O_3 in hydrochloric acid. J. Chem. Phys. 23: 1961 (1955).

(8) Gianola, U.F. Damage to silicon produced by bombardment with helium ions. J. Appl. Phys., 28: 868 (1957).

15. Other processes which might be expected to give rise to higher corrosion rates under irradiation have little or no supporting evidence. Two of these processes are the production of short-lived chemically active species in the irradiated solution and failure of the metallic oxide film by transformation of small areas which act as nuclei for failure of the whole film.

16. It is now reasonably certain that the major contribution to the enhanced in-pile corrosion is due to bombardment of the protective zirconium oxide film by the very energetic fission recoil fragments. The mechanism by which they achieve this remains the subject for further investigation.

17. From the point-of-view of reactor design, there is a limited number of ways of attempting to reduce the corrosion to an acceptable rate. There are only three main methods of approach and these will be described very briefly below.

(a) Control of solution composition.

18. Combination of the facts that out-of-pile corrosion is relatively unaffected by solution composition and that fission fragments are probably responsible for increasing the corrosion rate suggests that any solution undergoing fission may have the same ultimate effect. Moreover the same argument might apply to dilute aqueous slurry fuel systems. It is true that in the latter some fission fragment energy will be absorbed in the solid fuel particles, but for a slurry of highly enriched fuel particles of diameter considerably smaller than the fission fragment range, and containing no inert diluent, it is possible for some 80% of the energy to be deposited outside the particles(9). The rate at which fission fragment energy deposition occurred in the zirconium oxide film would then be little different from the case of a fission solution.

(b) Metallurgical methods.

19. Little success has been achieved to-date with modification of alloying additions to the zirconium. Additions of elements which either change the structure of the protective oxide film or affect diffusion characteristics in some other way may give improved corrosion resistance and experimental work is being pursued along these lines.

20. An alternative metallurgical protection method which is being considered is the cladding of the internal surface of the zirconium alloy core vessel with a more resistant metal. The corrosion rate of titanium at a solution power density of 15 kW/litre is only 2 mil/year and there appears to be a much lower dependence on power density than for zirconium alloys(3).

21. Methods have been devised for the successful application of a thin titanium sheet to a thicker zirconium sheet and good bonding characteristics are obtained. The primary factor which prevents the building of a

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(9) A fuller discussion of this aspect of slurry systems appears in the paper by Dawson, Long, Moseley and Sowden, The possibility of the direct application of fission recoil fragment energy to industrial chemical processes. Second Int. Conf. on the Peaceful Uses of Atomic Energy A/Conf.15/P/76 (1958).

satisfactory core vessel of this nature is the relatively high neutron absorption of titanium. This implies that only very thin layers may be tolerated, perhaps 0.010 inch maximum.

22. Because of the good corrosion resistance of titanium there is some incentive to investigate possible methods of producing separated ^{50}Ti, which occurs at about 5% abundance in natural titanium. Since the neutron absorption cross section of ^{50}Ti is a factor of 40 less than the natural mixture, it would be possible to build the complete core vessel of titanium with no greater neutron loss than if it were built of zirconium. Estimates have shown that separation of this isotope by gaseous diffusion would be far too expensive, but there remains the possibility of developing an efficient and cheap chemical exchange process. The remaining 95% of the titanium could still be used on the commercial market in the normal way, although the quantity involved would be relatively small. If this problem of isotope separation could be overcome, there is a good prospect of constructing a satisfactory corrosion-resistant core vessel to withstand a solution power density of 15 kW/litre. Experimental evidence is not yet available to show whether the corrosion rate would be acceptable at higher power densities.

23. Niobium has a rather lower neutron cross section than titanium and it could be used as a core vessel cladding in thicknesses up to 0.06 inch. The small amount of evidence available suggests that its corrosion resistance might be several times better than zirconium alloys under irradiation. Unfortunately, relatively large amounts of uranium are adsorbed from solution by the niobium oxide film; this could result in instability of the solution and would increase the rate of fission fragment energy deposition at the metal/oxide interface. We have measured the uranium adsorbed on niobium specimens from high temperature uranyl sulphate solutions out-of-pile by means of subsequent radioactivation. Under conditions where the amount absorbed in zirconium and titanium dioxide was below the limit of detection ($\sim 1 \mu g/cm^2$) the niobium carried uranium up to $250 \mu g/cm^2$. If the uranium is assumed to be uniformly distributed throughout the oxide film, this amount corresponds to 10% uranium in the film. If this deposition can be reduced by alloying the niobium, we may have a more corrosion resistant alternative to zirconium alloys for the neutron window.

(c) Physical control.

24. If it is accepted that increased corrosion under irradiation is due to fission fragment damage of the metallic oxide film, it may be possible to develop a physical protection method. This would take the form of a water film over the inside wall of the core vessel. The water film would require to be about 0.02 inch thick to screen the core vessel wall completely from the effects of the fission fragments. The water film could be obtained using a double-walled core vessel, the inner wall being porous and fed with a supply of pure D_2O from between the walls(10). The porous wall could be

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(10) Spence, R. Porous lining for aqueous homogeneous reactor to minimise corrosion. U.K. Patent Application No. 15169/56.

sintered zirconium or titanium. Apart from the construction difficulties which this would involve, the complexity of operation of the reactor would be increased by the necessity to maintain pressure balancing between three, rather than two, separate circuits (the pressure in the D_2O inter-wall feed must always be higher than the core circuit pressure to prevent access of fissile solution to the porous wall).

25. Further experimental work is required before it will be possible to determine which of the suggested methods of attempting to reduce the corrosion problem is likely to be the most suitable.

1.2 Nitrate systems

26. We have investigated the feasibility of using nitrate solutions in homogeneous aqueous reactors. The nitrate is the only thorium salt with sufficient solubility for consideration as a solution blanket for the two-zone reactor. It was thought worthy of investigation, therefore, as a possible means of eliminating handling difficulties encountered in the thoria slurry blanket. Because of the high nitrate concentration required in the blanket, the naturally occurring mixture of nitrogen isotopes would give too high a neutron absorption and it would be necessary to use the low neutron absorbing isotope, ^{15}N. There is a relatively cheap process available for separation of this isotope from the natural nitrogen mixture(11).

27. Nitrate solutions have also been considered for use as a core solution of a two-zone reactor, or as the working fluid of a single-zone burner reactor. The considerations of corrosion under irradiation discussed in Section 1.1 imply that probably there would be little advantage in substituting a nitrate for a sulphate solution. Nevertheless there may be other reasons for preferring the nitrate (for instance solution thermal stability) and it appears to be one of the few possible solutions which might be feasible for plutonium utilisation (Section 1.3).

28. Primarily our experimental work has been concerned with radiation stability of the nitrate ion. Solutions were sealed in evacuated silica ampoules, and irradiated in BEPO at a flux of about 10^{12}n.cm^{-2}sec^{-1}; after irradiation, gas analyses were carried out for H_2, O_2, N_2, N_2O, NO and CO_2, and solution analyses for NO_2^- and H_2O_2.

29. Three types of solutions were used:

(a) $Ca(NO_3)_2$ solutions over a nitrate concentration range 15.9 M. - 0.037 M.(12). Calcium undergoes insignificant interaction with pile neutrons, and energy deposited is therefore exclusively from the neutron plus gamma flux of the pile. Anderson[13] has developed a calorimetric

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(11) Spindel, W., and Taylor, T.I. Separation of nitrogen isotopes by chemical exchange between NO and HNO_3. J. Chem. Phys. 23: 981 (1955).

(12) Sowden, R.G. The effect of mixed fast neutron-gamma irradiation on calcium nitrate solutions. U.K. Atomic Energy Authority Report, A.E.R.E. C/R-2197 (1957).

(13) Anderson, A.R. Calorimetric measurement of energy absorption from reactor radiation in BEPO. U.K. Atomic Energy Authority Report A.E.R.E. C/R-2253 (1958).

technique for correlating energy deposition with thermal neutron dose in BEPO, and his figures were used to calculate G values.

30. The main products of irradiation (energy deposition extending to 7×10^{22} eV/g.soln.) were nitrite, hydrogen and oxygen, with small amounts of nitrogen from the more concentrated solutions: G_{N_2} for a solution 9.4 M. in nitrate ion was $\sim 3 \times 10^{-3}$. Nitrite and oxygen yields exhibited a scattered variation with dose, though the ratio of the two products was roughly constant. This might be explained by the fact that temperature during irradiation varied from 70 to 85°C., depending upon pile position, and that temperature affected nitrite back-oxidation. Indeed, maintaining the temperature of a 9.4 M. solution at 170°C. during irradiation reduced the nitrite yield some 3-4 orders of magnitude. Added acid also reduced the yield.

31. Hydrogen yields were found to be linear with dose and to depend upon $[NO_3^-]^{\frac{1}{3}}$. The significance of this result has been discussed elsewhere(14). Since it has little effect upon the design of a nitrate reactor blanket it will not be discussed further.

(b) $Ca(NO_3)_2$ solutions similar to those in (a) were irradiated, but impregnated with sufficient $U^{235}O_2(NO_3)_2$ to ensure that, in the BEPO thermal flux, >95% of the energy deposited was from fission recoil fragments(15). G-values were calculated assuming a fission cross-section for U^{235} of 580 barns, and recoil kinetic energy release per fission of 160 MeV.

32. Fission recoil energy deposition extended to 5×10^{21} eV per g. of solution. The main products were hydrogen, oxygen and nitrogen, with smaller amounts of carbon dioxide and, in the case of concentrated solutions, nitrous oxide. Some precipitation of UO_4 was experienced in more dilute solutions, but this was prevented subsequently by adding about 100 p.p.m. of Fe^{3+} to catalytically decompose hydrogen peroxide. No peroxide, and only traces of nitrite were found in solution at the end of an irradiation.

33. Nitrogen yields were more than an order of magnitude greater than those observed from fast neutron-gamma irradiation. Stoichiometry represented by the equation

$$2HNO_3 \rightarrow H_2O + N_2 + \frac{5}{2}O_2 \qquad \text{..........(1)}$$

was obeyed well at higher concentrations, but at low concentrations carbon dioxide formation had to be considered in obtaining a reasonable balance between oxidised and reduced species.

34. Figure 2 shows a plot of G_{N_2} vs $[NO_3^-]$, which includes the

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(14) Sowden, R.G. The effect of nitrate ion on the yield of hydrogen from water radiolysis. J. Amer. Chem. Soc., 79: 1263 (1957).

(15) Sowden, R.G. and Lynde (Miss) E.M. The effect of fission recoil energy on calcium nitrate solutions. U.K. Atomic Energy Authority Report, A.E.R.E. C/R-2480 (1958).

present data, those recently published by Boyle and Mahlman(16) on the $Th(NO_3)_4$ - $U^{235}O_2(NO_3)_2$ system, and those of Bidwell(17) obtained from experiments with the Los Alamos water boilers. The continuity of the curve indicates that cation variation has little effect on nitrogen yields. Our data were obtained at 80°C., while the American data correspond to temperatures ranging from 37°C. to 300°C.; temperature has therefore no significant effect on G_{N_2}. Below a nitrate concentration of 4 M., nitrogen yields can be expressed by the empirical relationship

$$G_{N_2} = 0.004 [NO_3^-]^{1.5} \qquad \ldots\ldots\ldots\ldots(2)$$

(c) Thorium nitrate solutions.(18)

35. The thorium nitrate solution used for irradiation was 11.8 M. in nitrate ion (corresponding to 650 g. Th per Kg. water). It was anticipated that the results could be explained in terms of the experience gained in (a) and (b). However it was found that substantial amounts of nitrogen were produced which could be related neither to the thermal neutron flux nor to the fission energy arising from the small amounts of U^{233} produced. Although no quantitative correlation could be made, irradiations within a cadmium shield and inside a hollow uranium slug indicated that fast fission of thorium was the causative factor. Boyle and Mahlman do not report any anomalous behaviour on irradiating $Th(NO_3)_4$ solutions without added U^{235}, but the fast neutron spectrum could be very different for the two reactors employed.

36. The results obtained show clearly that decomposition of nitrate ion to nitrogen by fission recoil energy is the chief factor to be considered in the assessment of nitrate systems. G_{N_2} values may be readily applied to estimating the seriousness of the problem in both blanket and core.

37. Let us consider a reactor solution in which power is generated at a density of (P)MW/litre. Power from fission recoil kinetic energy dissipation will then be ~ 0.8 P $MW.l^{-1}$, and since 1 MWhr. $\equiv 2.25\times10^{28}$ eV, the rate of nitrogen production will be

$$\frac{0.8P\times2.25\times10^{28}\times10^{-2}}{6.03\times10^{23}} G_{N_2} \text{ moles } hr^{-1}l^{-1}$$

$$= 300\ P.G_{N_2} \text{ moles } hr^{-1}l^{-1}$$

$$\sim 240\ P.G_{N_2}\ ft^3(S.T.P.)hr^{-1}l^{-1}$$

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(16) Boyle, J.W. and Mahlman, H.A. Radiation-induced decomposition of thorium nitrate solutions. Nucl. Sci. Eng., 2: 492 (1957).

(17) Bidwell, R.M., King, L.D.P. and Wykoff, W.R. Radiolytic yields of nitrogen and hydrogen in water boilers. Nucl. Sci. Eng., 1: 452 (1956).

(18) Sowden, R.G. Thorium nitrate as a breeder blanket for the H.A.R. Part 2. Radiation stability. U.K. Atomic Energy Authority Report, A.E.R.E. C/R-2196 (1957).

Hence if V is the circuit volume at power, the total rate of nitrogen production is

$$R_{N_2} = 240\ P.V.G_{N_2}\ ft^3(S.T.P.)hr^{-1} \qquad \ldots\ldots\ldots.(3)$$

38. The Harwell design study of a 100MW(E) two-zone H.A.R.(1) has provided blanket specifications of a thorium concentration of 880 gm.l^{-1}, and a power generation (PV in equation 3) of 92 MW(T), with a U^{233} concentration at equilibrium of 2.6 g.l^{-1}. If the blanket is of thorium nitrate solution, the concentration will be 3.8 M, and about 2M.HNO_3 will be required to suppress hydrolysis up to 300°C.(19).

39. The total nitrate ion concentration will therefore be ~17 M, and from Figure 2 a safe lower limit for G_{N_2} can be fixed at 0.07. Substituting in equation (3),

$$R_{N_2} \sim 1700\ ft^3(S.T.P.)hr^{-1}$$

In the reference design(1) the blanket circuit volume is 18,400 l, which corresponds to a nitrate inventory of 3.2×10^5 moles, and the above rate of decomposition would necessitate "refixing" of all the blanket ^{15}N more than once weekly! This situation could only be improved either by reducing the $Th(NO_3)_4$ concentration and hence G_{N_2}, or by rapid extraction of Pa^{233} to reduce the blanket power. Even if the first solution to the problem could be accepted on nuclear grounds, there would still be a limitation due to the fact that more acid is required for thermal stability as $[Th^{+4}]$ decreases,(19) and it is doubtful if G_{N_2} could be reduced more than a factor of two or three by this device. The second solution seems to be so difficult that any advantages of a solution blanket over a slurry would be lost. We therefore conclude that a thorium nitrate (^{15}N) blanket is not a practicable possibility.

40. The core situation, however, shows greater promise. Here the A.E.R.E. design study figures are PV = 306 MW(T) with a uranium concentration of 0.004 M, and an acid concentration of 0.02 M. required to ensure thermal stability at operating temperature. Secoy has shown(20) that dilute solutions of uranyl nitrate exhibit hydrolytic instability above 260°C., but little data is available on the suppression of hydrolysis by added acid. Assuming approximately twice the acid concentration required for operational stability in the sulphate case, the total nitrate molarity would be 0.05, and from equation (2),

$$G_{N_2} \sim 4 \times 10^{-5}$$

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(19) Sowden, R.G. and Jones, P.G. Thorium nitrate solution as a breeder blanket for the H.A.R. Part 1. Thermal stability. U.K. Atomic Energy Authority Report, A.E.R.E. C/M-298 (1956).

(20) Secoy, C.H. Survey of homogeneous reactor chemical problems. International Conference on the Peaceful Uses of Atomic Energy, Geneva, A/Conf.8/P/821 (1955).

Substituting in equation (3) we have

$$R_{N_2} = 3.6 \text{ moles.hr}^{-1} = 2.8 \text{ ft}^3(\text{S.T.P.})\text{hr}^{-1}$$

Assuming the stoichiometry of equation (1), nitrogen-oxygen mixture will be evolved at the rate of about 10 ft^3(S.T.P.)hr^{-1}. It may presumably be flashed off at intervals, after recombination of D_2 and O_2, scrubbed free from activity, and mjected to atmosphere. DNO_3 make-up would be required at the rate of about 1.5 tons per annum (with some flashing-off of D_2O as required by equation (1)). Estimation of the costs involved are too speculative at this stage, but the rate of nitrate decomposition alone would not appear to exclude the use of nitrate solution fuels. Recent work has shown, however, that there may be little advantage to be gained by using uranyl nitrate rather than the sulphate, and plutonyl nitrate probably has insufficient thermal stability.

1.3 Plutonium solution fuels

41. The United Kingdom, in embarking upon an extensive programme of electricity production from natural uranium, will ultimately be producing large quantities of ^{239}Pu as a by-product. We have investigated some of the chemical aspects of employing this plutonium as a fuel for H.A.R. systems.

42. The plutonium fuelled reactor could utilise either a plutonium aqueous solution or a dilute suspension of an insoluble compound. Plutonia suspensions are discussed in Section 2.2; in the present section we are concerned with possible solution fuels.

43. In order to be acceptable, the primary requirements that a solution must fulfil are:

Plutonium salt soluble in the range 1-10 g/litre.
Thermally stable up to ~300°C.
Radiation stable.

The experiments reported here were performed to obtain information on the first two of these requirements.

44. For similar reasons to those which apply to uranium solutions (neutron absorption and corrosion limitations) the choice of anion is restricted to nitrate, carbonate and sulphate. The situation is more complicated for plutonium owing to the greater stability of the lower oxidation states in aqueous solution. The most stable oxidation state in any particular set of conditions will depend upon a number of factors, such as oxidation-reduction potentials, complex formation, disproportionation reactions and hydrolysis. A complete assessment is not possible at the present stage since only a very small amount of information on these topics is available above 70°C.

45. There is negligible hydrolysis of trivalent plutonium solutions at pH 5 at room temperature. It seems reasonable to suppose that high temperature hydrolysis might be suppressed at pH 2. However, since quadrivalent plutonium is precipitated as the hydroxide at the latter acidity,

it must be ensured that the plutonium remains in the trivalent state. Nitrate ion is known to be able to oxidise Pu(III) and Pu(IV) to hexavalent state and the reaction is very fast at temperatures as low as 100°C.(21) Hence trivalent plutonium nitrate solution may be eliminated from further consideration.

46. Trivalent plutonium sulphate solution has been found to have a negative coefficient of solubility, similar to that of the trivalent lanthanides. In 0.025 M. sulphuric acid, the solubility decreases to a value much less than 1 g/litre at 215°C.(22) Such solutions are not, therefore, suitable for reactor application.

47. Trivalent plutonium carbonate is appreciably soluble in concentrated alkali carbonate solutions. At high temperatures, however, a large over-pressure of carbon dioxide would be required to prevent hydrolysis and it might also be difficult to maintain reducing conditions in the system.

8. Failing the availability of a suitable trivalent plutonium solution we may examine the possibility of quadrivalent solutions. Quadrivalent plutonium appears to require a much higher acidity than Pu(III) or Pu(VI) to prevent hydrolytic precipitation at high temperatures. It has been shown, for instance, that in the plutonium concentration range 4-16 g/litre irreversible precipitation occurs above approximately 190°C. in a solution of 0.5 M. sulphuric acid(22). To suppress hydrolysis up to 300°C. would evidently require a very acid solution. Containment problems would then become more severe.

49. It is interesting to examine how close an analogy it is possible to draw between plutonyl and uranyl solutions. The uranyl ion is relatively stable at high temperature, uranyl sulphate is stabilised at 300°C. by the presence of 0.02 M. sulphuric acid. Experiments have shown, however, that Pu(VI) in 0.05 M. sulphuric acid is reduced to Pu(IV) at a measurable rate even at 100°C. This cannot be attributed solely to reduction by hydrogen peroxide formation from the effect of alpha particles on water(23). It is necessary to postulate that water itself acts as the reducing agent, the process probably proceeding in two stages:

$$\mathrm{Pu(VI)} + \mathrm{H_2O} = \mathrm{Pu(V)} + \mathrm{H^+} + \mathrm{OH}$$

$$2\,\mathrm{Pu(V)} = \mathrm{Pu(IV)} + \mathrm{Pu(VI)}$$

There is no fundamental reason why this reduction should not have been

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(21) Connick, R.E., *Oxidation states, potentials and equilibria of oxidation-reduction reactions of plutonium.* National Nuclear Energy Series, IV-14A, McGraw-Hill Co., Chapter 8 (1954).

(22) Grant, D.W. and Glanville, D.E. *The hydrolytic behaviour of plutonium ions in sulphuric acid.* U.K. Atomic Energy Authority Report No. A.E.R.E. C/R-2155 (1957).

(23) Glanville, D.E. Unpublished work.

observed previously in work at room temperature, but presumably the rate of reaction was then too low.

50. In principle, Pu(VI) sulphate could be stabilised against this reduction by decreasing the acid concentration, but it is probable that the minimum acid required to suppress hydrolysis would be close to the maximum acid required to suppress reduction. It would consequently be very difficult to ensure the thermal stability of such a fuel solution.

51. It is possible that sufficiently oxidising conditions could be obtained in a nitrate system to retain plutonium in the hexavalent state. Experiments on the thermal stability at elevated temperatures have shown, however, that hydrolytic precipitation takes place unless the solution contains considerably more acid than would be required in the corresponding uranyl solution(23). For instance, plutonium at a concentration of 10g/litre is precipitated irreversibly in silica tubes at temperatures in the range 200-250°C. if the solution is 0.1 M. in nitric acid. Increasing the acidity to 1.0 M. does not appear to increase the precipitation temperature above 250°C. Work is being continued on this system to determine more precisely the conditions for thermal stability, particularly the effect of high oxygen overpressures.

52. It is known(24) that Pu(IV) is oxidised to Pu(VI) in concentrated carbonate solutions at 100°C. There is no information at the present time concerning the high temperature thermal stability of Pu(VI) in alkali carbonate solutions. Unless the alkali carbonate is present at high concentrations (> 3 M.), difficulty is experienced in maintaining the plutonium in solution at room temperature(25). This appears to be due to reduction of Pu(VI) to Pu(IV) by hydrogen peroxide arising from the alpha particle bombardment of water and would present severe problems in the storage of such solutions. A further disadvantage would be that given also for the Pu(III) carbonate system: namely, a high additional working pressure of carbon dioxide.

53. In summary it would appear that the choice of possible plutonium solution fuels is much more restricted than for uranium fuel solutions. Probably the greatest possibility of plutonium utilisation in an H.A.R. system lies in the use of a slurry of plutonium dioxide as discussed in Section 2.2.

2. AQUEOUS SLURRIES

54. Slurry systems have a number of different possible applications in homogeneous aqueous reactors. Chemical investigations at A.E.R.E. have covered the preparation and properties of slurries of ThO_2, UO_3 and PuO_2.

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(24) Yakovlev, G.N. and Gorbenko-Germanov, D.S. Coprecipitation of Am(V) with double carbonates of U(VI) and Pu(VI) with potassium. International Conference on the Peaceful Uses of Atomic Energy, Geneva, A/Conf.8/P/677 (1955).

(25) Grant, D.W. Unpublished work.

Our rheological studies have been confined to the thoria system. Recent work on the latter is discussed in Section 2.1, and preliminary work on plutonia is described in Section 2.2.

2.1 Thoria slurries

55. It was shown in Section 1.2 that a thorium solution blanket for a two-zone breeder H.A.R. would be impracticable. We are forced, therefore to consider a slurry system; the required concentration would be in the region of 1000 g. ThO_2/litre D_2O. The experimental work has also covered concentrations down to 300 g. ThO_2/litre, since this would be of interest for a single-zone H.A.R. using a $^{233}U/^{232}Th$ fuel system.

56. It was considered necessary to examine these slurries on a fundamental basis to determine what would be the variables which exert a controlling influence on the handling characteristics.

57. Studies have been made of the variation in properties of thoria with method of preparation, impurity levels and additives. Since, however, the results do not differ significantly from previously published work at Oak Ridge(26), they will not be discussed in detail.

58. The physico-chemical problems presented by a slurry are mainly those of the ionic solid-aqueous phase interface. Kruyt(27) considers that a slurry may be regarded as a lyophobic colloid, with a tendency to settle because of large micelle size, and thus the techniques and modes of thought of colloid chemistry are useful guides to the study of slurries.

59. A slurry may be dispersed or flocculated, its condition depending largely upon the electrical condition of the oxide surface. A dispersed slurry settles slowly to a dense dilatant bed which is difficult to redisperse; whereas a flocculated slurry settles more rapidly to a loose, readily dispersible bed. Redispersion considerations, therefore indicate that a flocculated slurry would be easier to handle, but Lyon(28) has proposed that flocculation is one of the factors contributing to caking. Thus, although it is not possible to decide definitely at this stage whether flocculation or dispersion is required, it is clearly desirable to be able to define conditions under which the degree of flocculation or dispersion can be predicted.

60. A physical quantity which has been related to stability is the ζ-potential. Powis(27) proposed that flocculation in an oil-water suspension occurred when the potential fell below a critical value, and the concept has since been applied to lyophobic colloids, though its validity has

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(26) McBride, J.P., Information on slurries. U.S. Atomic Energy Commission Report No. CF-57-3-21.

(27) Kruyt, H.R., Colloid Science, Vol.1, Elsevier (1952).

(28) Lyon, R.N. The choice of thorium oxide slurries for the prevention of caking in circulating systems. U.S. Atomic Energy Commission Report No. ORNL-57-4-77 (1957).

been disputed by some authors(29). We have made some observations on the dispersion of thoria in various HCl solutions, and these indicate that the 'critical ζ-potential' concept is inapplicable to this system. Thoria (prepared by dropwise addition of 1 M. oxalic acid to 1 M. thorium nitrate solution at 70°C., followed by calcination at 900°C.) was used to prepare suspensions (10 g./litre) in water and HCl solutions. Figure 3 is a photograph of the suspensions after five hours settling, following vigorous shaking, and shows clearly that dispersion is obtained only at HCl concentrations greater than 10^{-3} M. If it is assumed that the particle size distribution of thoria prepared by this method contains $\sim 6\% < 1$ micron diameter(31), then Figure 3 also shows that "fines" are removed by flocculation at low hydrochloric acid concentrations since Stokes' law indicates that 1 micron particles will take 5 hours to settle 10 cm. at 20°C.

61. Measurements were made of ζ-potentials by electrophoresis of very dilute (<10 mg./litre) suspensions.

HCl (M.)	ζ (mV)
0	>20
10^{-6}	47
10^{-5}	48
10^{-4}	20
10^{-3}	9
10^{-2}	-10

They show the same trend as the data of Anderson(30), who also observed a depression of ζ at higher HCl concentrations. Thus dispersion appears to be related to a low value of ζ, contrary to the concept of Powis. It should be pointed out that in Figure 3 only the suspensions with HCl concentrations 0, 10^{-3}, 20^{-2}, may be assigned the ζ-values of the table. Analysis of the supernatant liquid indicated that, in the other three cases, ion exchange on the thoria surface had increased the pH, and the solid was therefore in equilibrium with an HCl concentration lower than that indicated by the label.

Rheology

62. These slurries were expected to be non-Newtonian, i.e., to show viscosities dependent upon shear rate. Each slurry would then be characterised by a shear diagram and investigations have been made of the effect of a considerable number of variables on the latter. The experiments were performed using a simple vertical pipe-line viscometer in which slurry was transferred from a lower to an upper stirred vessel through one of a

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(29) Eilers, H. and Korff, J. The significance of the phenomenon of the electrical charge on the stability of hydrophobic dispersions. Faraday Society Discussions on the Electrical Double Layer (1939).

(30) Anderson, P.J. On certain ionic equilibria at the thoria electrolyte interface. U.K. Atomic Energy Authority Report No. A.E.R.E. M/R-2194 (1957).

(31) Aldred, V.D., Buxton, S.R. and McBride, J.P. Characteristic properties of thorium oxide particles. J. Phys. Chem., 61: 117 (1957).

number of small bore stainless steel pipes by a controlled air pressure applied to the lower vessel.

63. This design was chosen as one which might readily by adapted to high temperature and pressure operations. It was intended that while the bulk of the experimental work in determining the influence of fundamental properties could be confined to ambient temperatures and pressures, the results of this work should be confirmed at reactor operating temperatures. Furthermore, the apparatus could be designed to operate with small quantities of slurry so that it would not be necessary to prepare large quantities of any particular material in order to study variations in shear diagram with method of preparation.

64. Shear diagrams of a number of slurries are shown in Figures 4 and 5. From these it can be seen that the slurries are neither true Bingham plastics nor pseudo-plastics. They have a definite yield stress but the relationship between ($\delta V/\delta r$) and τ is not linear. Crawley and Kitzes(32) have shown that this type of shear diagram may be explained on the assumption that a fraction of the liquid medium of the slurry forms a lyosphere about the solid particles and increases the effective solids volume. As the thickness of this lyosphere varies with shear stress in the system, so the effective solids volume (and therefore the apparent viscosity) vary. Correspondence of the present data with those of the above authors is shown in Figures 6 and 7 where the results have been plotted as the ratio of lyosphere thickness to particle radius, t/a, against shear stress τ. In each case the data are in reasonable agreement with the equation.

$$\frac{t}{a} = c\tau^{-0.2}$$

obtained by the above authors with thoria slurries which had been circulated at high temperatures. The constant (c) characterises the various slurries. It is independent of concentration for a given slurry but insufficient data are at present available to enable an analysis of the dependence of the constant on other factors to be made. It is clearly affected by particle size as shown by comparison of the results for a given commercial thoria after pumping with the results for the same material in the "as-received" state (Figure 6). Some preliminary results of measurements of the effect of SO_4^{2-} ion on the shear stress diagram of a slurry, (which was deflocculated in the "as-received" state) show that (c) varies as the state of aggregation of the slurry solids changes, (Figure 8). This effect is being further investigated.

Loop studies

65. The study of the behaviour of slurries in pumped loops was under-

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(32) Crawley, P.R. and Kitzes, A.S. Rheological behaviour of thorium oxide slurries in laminar flow. Industrial and Engineering Chemistry, 49: 888-892 (1957).

taken in part to ensure that viscometer results could be correlated with the pressure drop-flowrate results from a loop system and in addition to study the variation in shear diagram of the slurry with changes occurring as a result of circulation. Further, other aspects such as the settling of slurries during flow and the general development and performance of slurry handling equipment would be covered in these operations. The applicability of the results of low pressure loop studies would be confirmed later in high pressure loops. For all loop studies, thoria available in quantity commercially (firing temperature 1100°C.) would be used on the assumption that its behaviour would be correlated with its rheological properties and fundamental properties.

66. Investigations of pressure drop and flow rate have been made to date under ambient temperature and pressure conditions. Early experiments(33) showed that, for slurries up to 600 g. ThO_2/litre in $\frac{3}{4}$ in. and 1 in. pipes, friction factor data plotted versus a Reynold's number using the viscosity of water at the working temperature and the density of the slurry were in reasonable agreement with the friction factor data for water in the same pipes plotted on a similar basis. Further studies at higher thoria concentration are in progress, in conjunction with studies of the shear diagrams of the material being pumped. In addition, the linear velocity at which the solids distribution ceases to be uniform across the diameter of a horizontal pipe has been observed using a gamma source and counter to scan the pipe diameter.(34) It has been found that the average velocities at which inhomogeneity is observed in 0.94, 1.18 and 1.74 in. I.D. pipes are 1.40, 1.42 and 1.46 ft/sec. and are independent of concentration. This method has been shown to be extremely sensitive; for instance, for a particular slurry no maldistribution was observed while circulating the slurry at a mean velocity of 1.49 ft/sec. in a 1.8 in. pipe for 2 hours, but inhomogeneity was observed in 10 minutes at 1.42 ft/sec.

67. A complete analysis of this phenomenon cannot be given until further experiments have been performed over a wider range of pipe lengths and diameters.

68. The final check of flowrates in the low pressure loop studies was by weigh tank measurement. A simple Venturi type meter however, has given good results when compared with the weigh tank. In addition, an electromagnetic flow meter (Altoflux Limited) has been shown to give excellent results. The usefulness of the latter type meter has resulted in the construction of a similar meter for operation at high temperature and pressure.

69. It has been found that the technique described by Hitchon(34) for

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(33) Hitchon, J.W. and Murdoch, R. The pumping of aqueous thoria slurries. U.K. Atomic Energy Authority Report No. A.E.R.E. CE/M-189.

(34) Hitchon, J.W. The use of a radiometric technique to investigate the settling of aqueous thoria slurries. U.K. Atomic Energy Authority Report No. A.E.R.E. CE/M-188.

measuring the homogeneity of a slurry in a pipeline may also be utilised to measure the concentration of slurry in the pipeline. A unit has been constructed for this purpose and it is intended that this method will be used in high pressure loop studies in preference to sampling techniques.

Sedimentation

70. The settling rates of commercial and a number of specially prepared thoria samples have been measured over a range of temperatures from 20°C. to 295°C. and a range of concentrations from 250 g. ThO_2/litre to 1500 g. ThO_2/litre, using a windowed autoclave. The results of this work(35) show a great increase in settling rate with increased temperature, and reduction in settling rate with concentration. There are marked differences between the different preparations, probably due to particle size differences. In only one case was a slurry observed to be partially deflocculated at low temperature; in this case the slurry became flocculated at high temperature and remained so on cooling.

71. Much work remains to be done before the behaviour of slurries in terms of the fundamental properties of the oxide can be stated with precision. The use of the Crawley-Kitzes equation should, however, allow the rheology of a slurry to be completely determined from a few viscometer measurements and it is possible that a study of the dependence of the constant in their equation may permit the rheology to be determined from more fundamental properties. It remains to show how turbulent flow data can best be related to the shear diagrams given by these relationships.

2.2 Plutonia slurries

72. We have shown in Section 1.3 that the outlook for the utilisation of plutonium in the form of a homogeneous solution reactor fuel is not promising. An oxide slurry system has a number of attractive features.

73. A slurry fuel provides the opportunity for a relatively wide range of concentration and constituent variation without the stability problems encountered in a solution fuel. Radiolytic gas production would be less in a slurry than in a solution system owing to absorption of some of the fission recoil fragment energy in the slurry particles. It would not be possible to utilise the internal recombination catalyst which has been developed for the uranyl sulphate solution and the choice of such a catalyst remains one of the problems of a slurry system. Even in a concentrated slurry of ThO_2, it has been shown that the slurry particles themselves do not have a sufficient catalytic activity for the recombination(36). The development of a suitable catalyst for addition to the system can be forseen, and some suggestions have been made already(37). A relatively dilute slurry of small diameter particles is expected to be much less erosive than the concentrated thoria slurry envisaged for the blanket of a two-zone breeder reactor.

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(35) Cheney, A.G. Unpublished work.

(36) Sowden, R.G. and Francis, K.E. The problem of catalytic recombination of radiolytic gas in the slurry blanket of the H.A.R. A.E.R.E. C/M-335 (1957)

(37) Morse, L.E. Catalysts for the recombination of radiolytic gases over thorium dioxide slurries. U.S. Atomic Energy Commission Report No. ORNL 57-1-117 (1957)

74. Our attention to date has been devoted to a preliminary study of some of the chemical problems associated with dilute suspensions of plutonium dioxide: the study may have to be extended to a PuO_2/ThO_2 system or PuO_2 in solid solution in an inert carrier oxide if the chemical engineering problems of very dilute suspensions are ultimately shown to introduce unexpected difficulties.

75. Experiments have been performed on the variation of physical properties of PuO_2 with method of preparation, including calcination of the oxalate, sulphate, iodate, nitrate and hydroxide. The results are summarised in Table I. Surface areas were measured by the B.E.T. method, and densities in carbon tetrachloride. Approximate particle size distributions were obtained visually using an optical projection microscope at a magnification of X1000.

TABLE I

Some physical properties of PuO_2

Method of preparation	Specific surface area m^2g^{-1}	Density $gm.cc^{-1}$	Tap density $gm.cc^{-1}$	Particle size distribution
Sulphate fired at 760°C.	39	11.32±0.06	2.0	Very uniform approx. 1-2 μ.
Iodate fired at 600°C.	31	10.15±0.13	1.3	Very uniform approx. 1-2 μ.
Oxalate fired at 500°C.	112	10.31±0.08	0.9	Wide range of particles 1-10 μ.
Nitrate fired at 500°C.	10	-	2.2	-
Hydroxide fired at 300°C.	Too low to measure	9.81±0.17	5.4	Large particles, brittle.

76. It is evident from the particle size observations that the sulphate, iodate and oxalate yield the most satisfactory products for a slurry. The sulphate density corresponds to the theoretical value within the experimental error, while those of the iodate, oxalate and hydroxide products are significantly below theoretical. The large particle size of the oxalate sample compared with its extremely high specific surface area indicates a very open structure relative to the sulphate preparation. This is supported by the effect of calcination temperature on specific surface (Figure 9); the structure apparently collapses rapidly on heating to temperatures above 500°C.

77. The effect of high temperature water on plutonium oxide from sulphate has been examined by heating a settled suspension in a static autoclave at 300°C. for 170 hours. The surface area showed no detectable change (from 33 to 32 $m^2/g.$) and microscopic observation confirmed no substantial alteration in particle size distribution. Examination for water retention on a quartz spiral thermogravimetric balance showed that >99.5% of water was expelled below 100°C. in air and there was no evidence of hydrate formation.

78. Hardness tests on a sulphate-prepared sample revealed that plutonia will scratch both quartz and chromium and is therefore at least as hard as thoria (7 on Moh's scale).

79. Apart from its possible effect upon slurry stability, the electrical condition of the surface of slurry particles may affect their tendency to adhere to container walls. Extensive plating-out on the walls of heat exchanger surfaces could be a serious problem, particularly in dilute slurry systems. In the A.E.R.E. design study reactor(1), a core circuit volume of 14,600 litres and a circuit surface area of 25,000 ft^2 imply that the uniform deposition of a layer of PuO_2 only one micron thick would reduce the concentration of a 2 g./litre slurry by nearly 80 per cent. An assessment of methods of overcoming this possibility must await further experimental work on the surface characteristics of dilute slurry particles.

80. Much more experimental work is necessary before a comprehensive assessment of the potentialities of PuO_2 slurries can be made. For instance, there is no evidence on the effect of irradiation upon the important parameters which determine slurry behaviour. Also the adsorption properties of the PuO_2 for fission and corrosion products are unknown. The work so far, however, has not shown that any serious difficulties would be encountered in a reactor system of this type.

Acknowledgements

81. The authors wish to thank Dr. J. Adam, Metallurgy Division, A.E.R.E., for the X-ray data used in Figure 1. Mr. K.E. Francis performed much of the experimental work discussed in the Section on PuO_2. The rheological data on thoria slurries are based upon unpublished work by Dr. H.A. Kearsey.

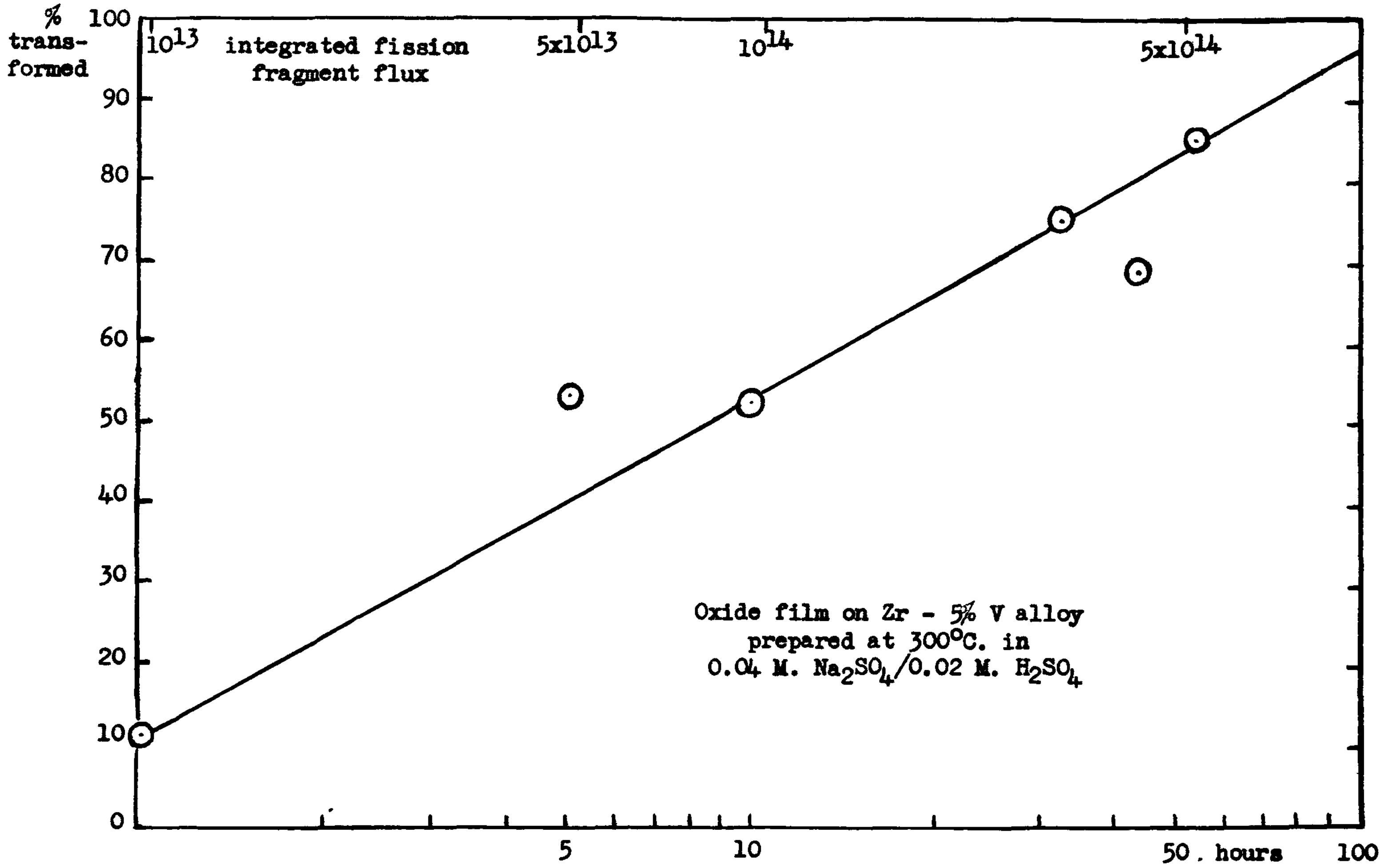

FIG. 1. FISSION FRAGMENT IRRADIATION OF ZrO_2 FILMS

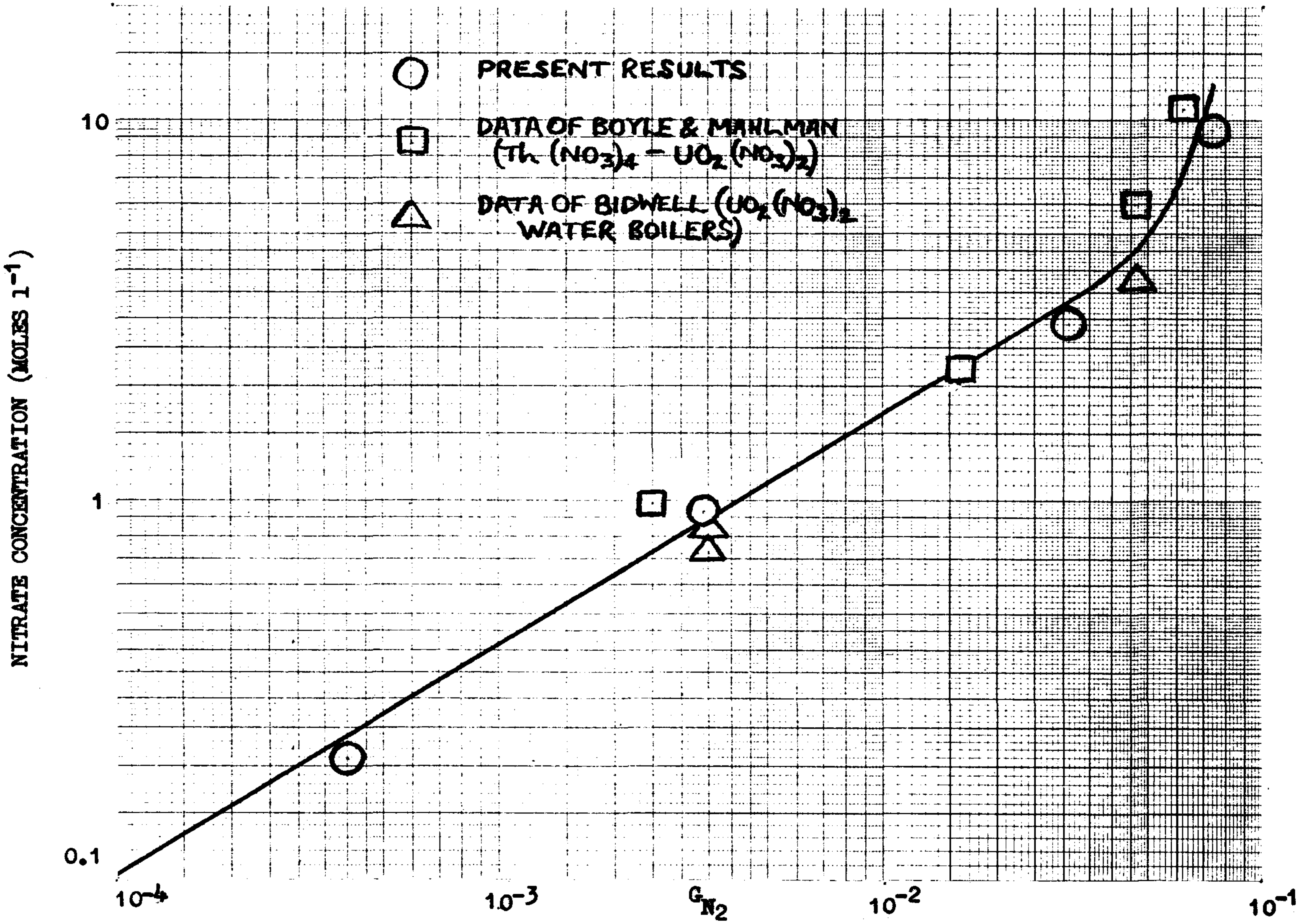

FIG. (2). LOG-LOG PLOT OF G_{N_2} Vs $[NO^-_3]$

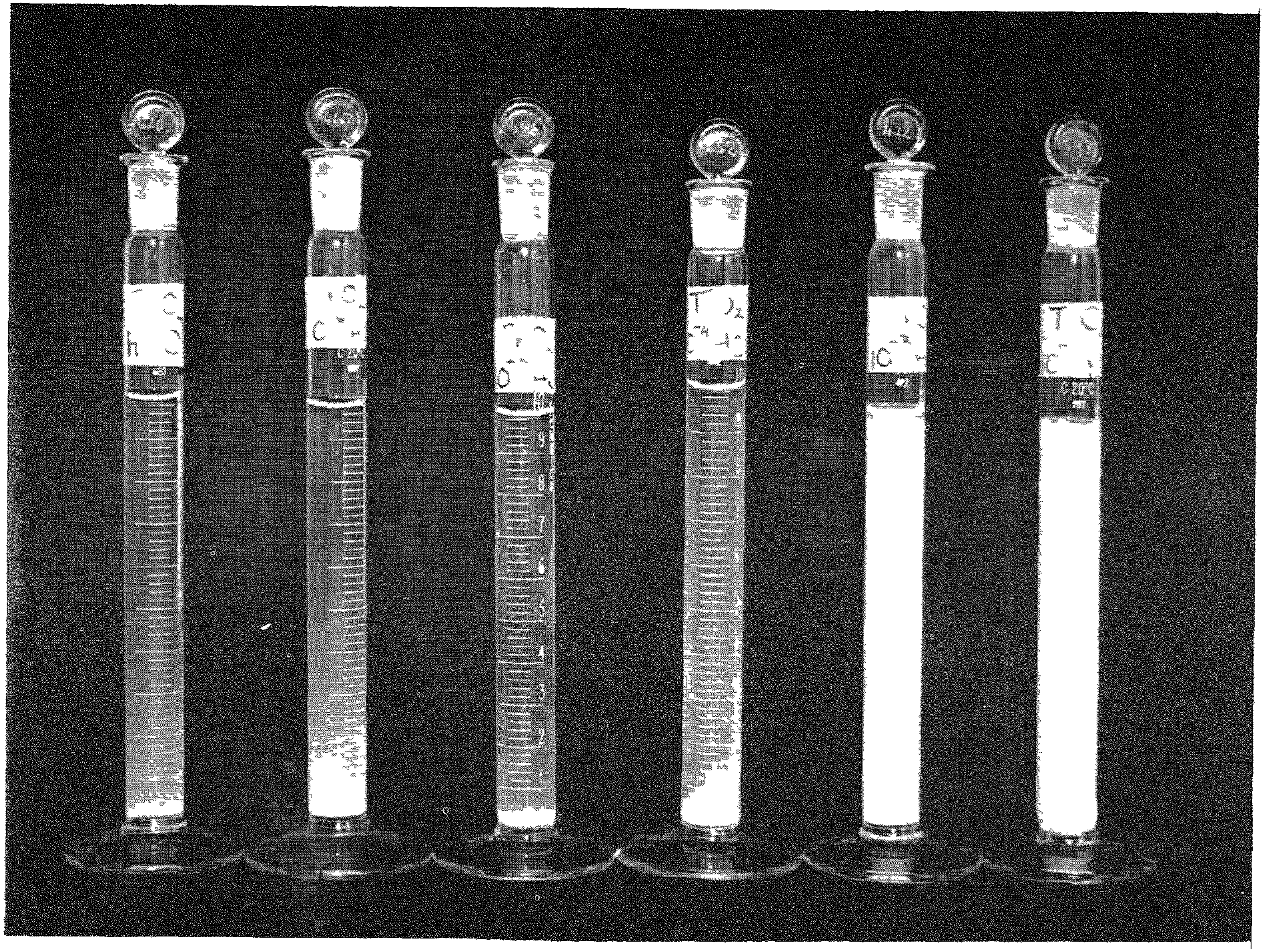

Fig. 3. Thoria suspensions (10 g/litre), with added HCl, after 5 hours settling time.

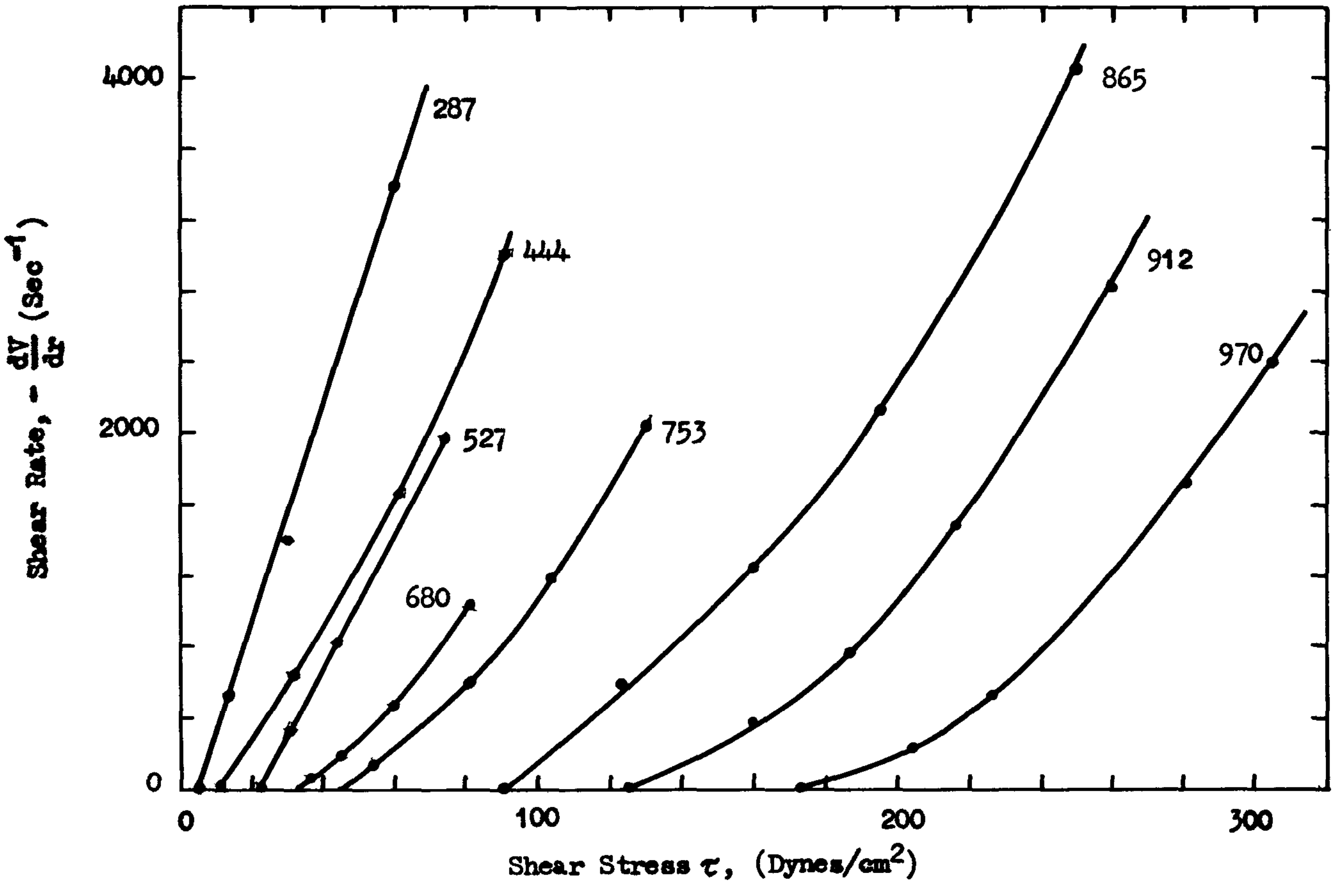

Fig 4. Shear Diagrams of Thoria Slurries.
Commercial Thoria, after circulation in Loop for 18 hours at 50°C.
Concentrations in Gms ThO_2/litre
Measurements at 25°C.

CONDITIONS OF PREPARATION

NO.		TEMPERATURES, °C.	
*	⁄	OXALATE PPTN	IGNITION
S1	S5	40	600
S2	S6	40	1000
S3	S7	100	600
S4	S8	100	1000

* PPTD. BY ADDITION OF $(COOH)_2$ TO $Th(NO_3)_4$

⁄ PPTD. BY ADDITION OF $Th(NO_3)_4$ TO $(COOH)_2$.

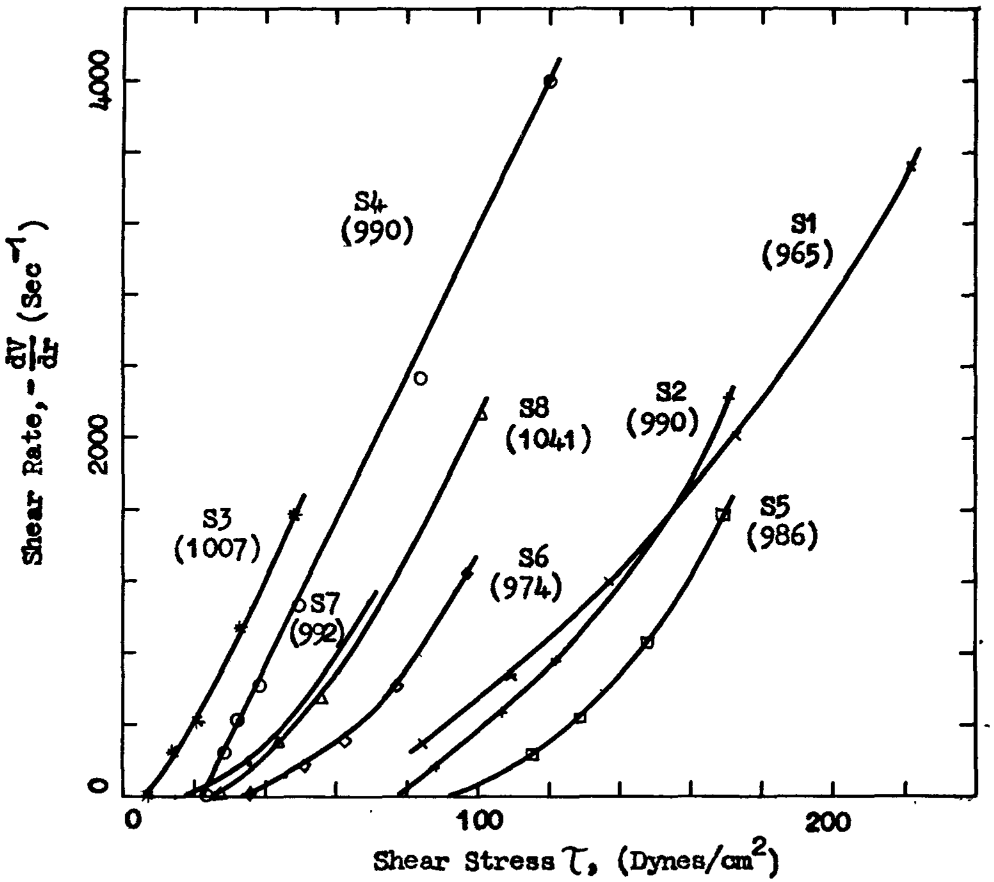

Fig. 5. Shear Diagrams of Thoria Slurries
Special Preparations of Thoria
Concentrations in Gms ThO_2/litre.
Measurements at 25°C.

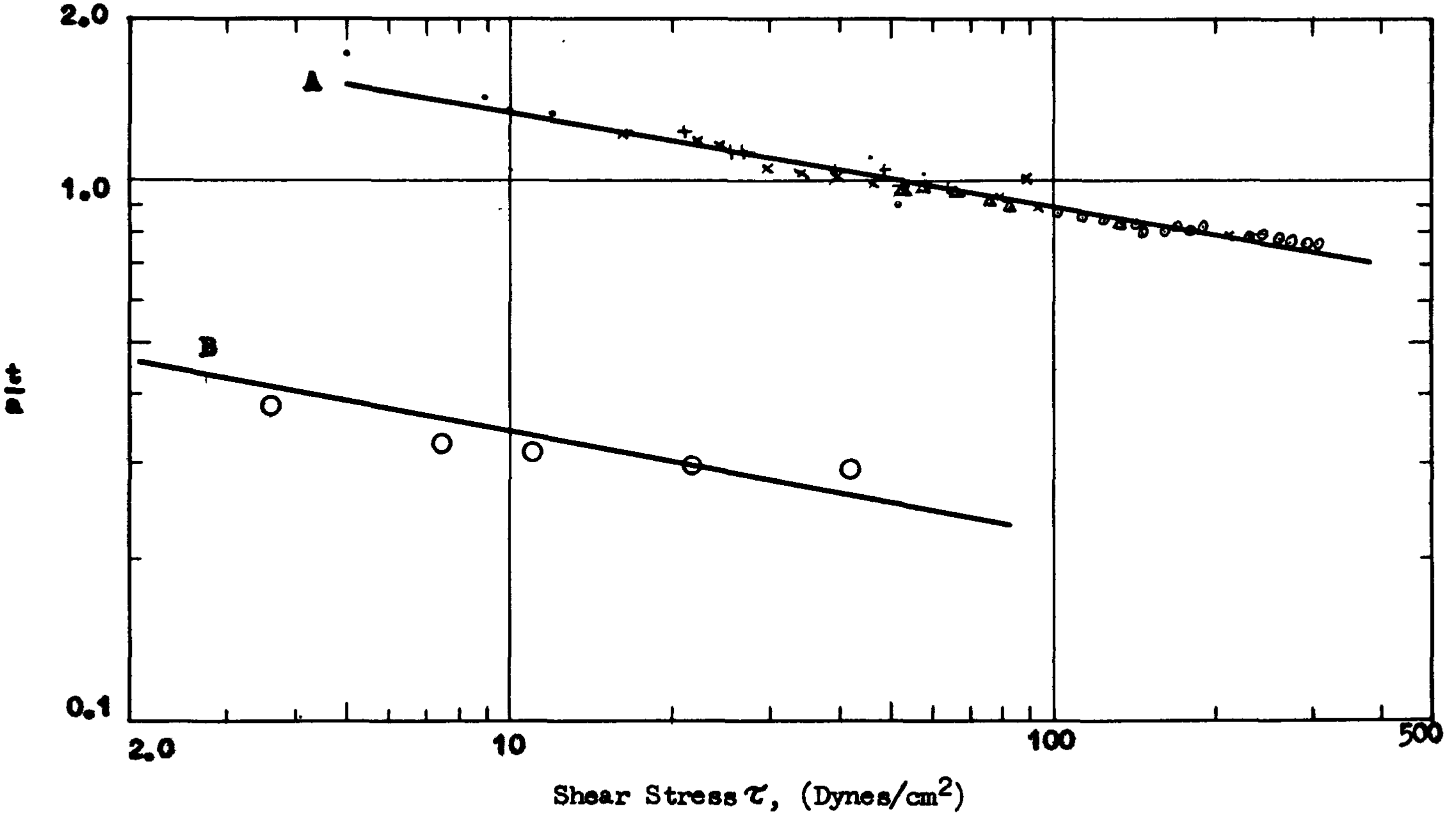

Fig. 6. $\frac{t}{a}$ vs. τ. Commercial Thoria.

A. After circulation in Loop for 18 hours. (Data from Fig. 4)

B. Before pumping.

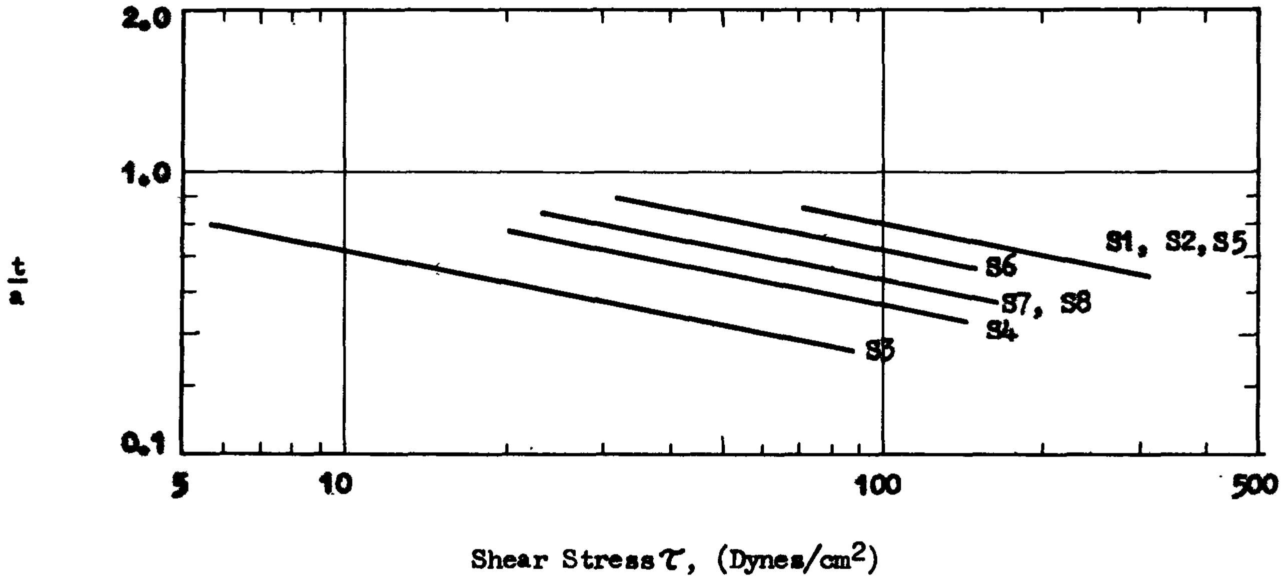

Fig. 7. $\frac{t}{a}$ vs. τ. Special Preparations of Thoria
(Data from Fig. 5)

Fig. 8. Shear Diagrams of Thoria Slurries.
As-Received Commercial Thoria.
Measurements at 25°C.

	A	B	C
Concentration (Gms ThO_2/l.)	1036	1024	983
Added Sulphate (p.p.m.)	0-300	450	600

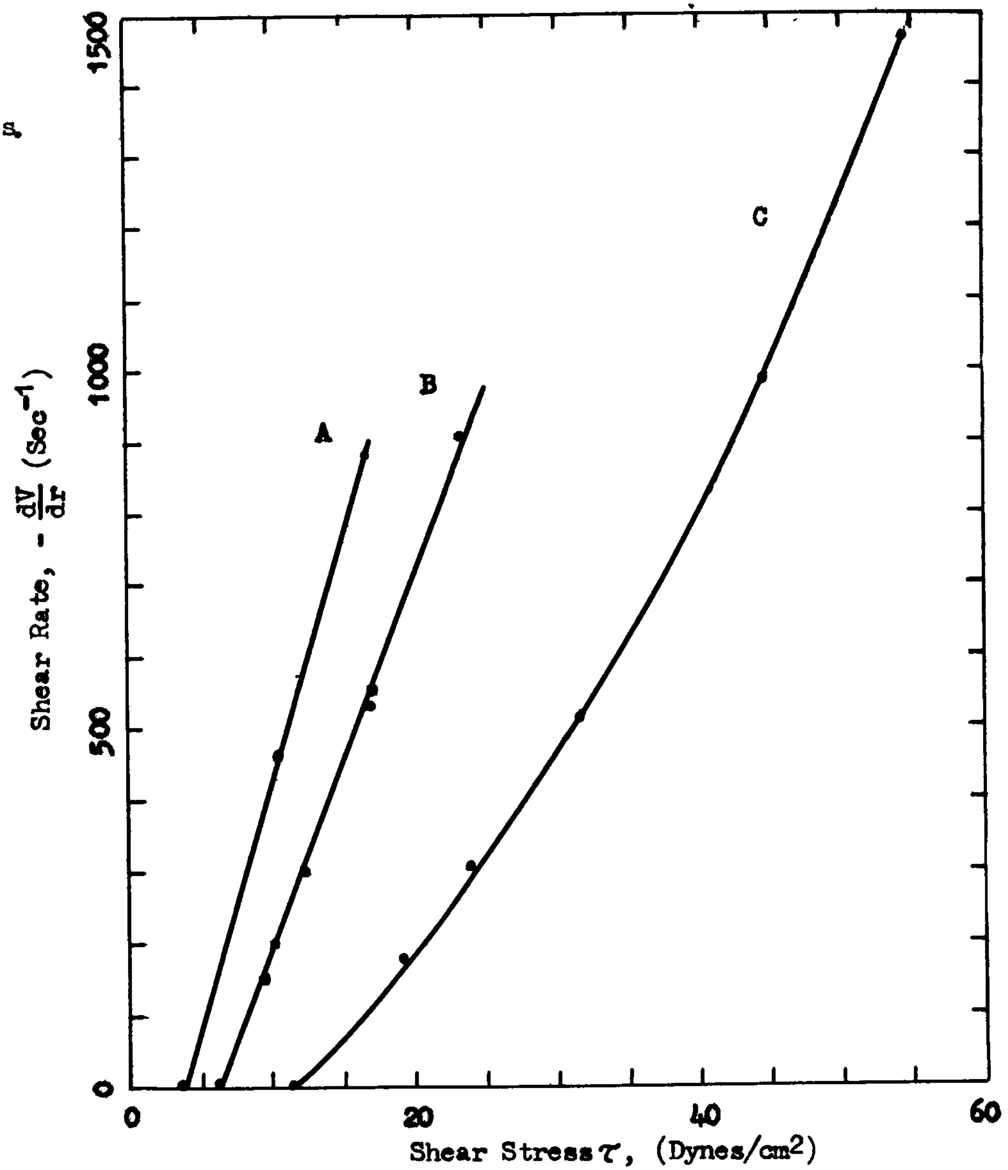

Fig. (9) Effect of calcination on surface area of two different PuO_2 samples.