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ABSTRACT

Methods of reducing the concentration of contaminants in mine water and in the acidic raffinate from uranium milling operations have been studied. Lime, limestone, caustic soda and lime-soda ash mixtures were compared as reagents for neutralising raffinates and for removing amines and heavy metals including radium from solution. All methods of neutralisation reduced contaminant levels significantly. Two-stage neutralisation using limestone in the first stage to pH 4, followed by second stage lime treatment appears to be an economically attractive approach. This method usually gave the lowest residual radium concentration provided the solids from the first stage were not removed before adding lime.

Radium can be further removed from neutralised raffinates or from mine water conditioned with sulphate by the addition of barium chloride to co-precipitate the sulphates of barium and radium. The concentration of radium was readily reduced to less than 3 pCi ℓ^{-1} by adding 10 mg Ba ℓ^{-1} raffinate. For mine waters conditioned to 0.01 M in sulphate, barium additions of 20 mg ℓ^{-1} were required to attain the same radium concentrations. Adsorption on barytes was also effective in removing radium from conditioned mine water and neutralised raffinates.

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AMINES; COPRECIPITATION; LIMESTONE; LIQUID WASTES; MILLING; MINING; ORE PROCESSING; PH VALUE; RADIUM; SODIUM HYDROXIDES; URANIUM ORES; WASTE PROCESSING

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1. INTRODUCTION

There are a number of possible sources of pollution in the mining and processing of uranium ore. These include radon and daughter products emitted during mining, crushing and grinding; pit water from mining operations; contaminated water from weathering of overburden, below-ore-grade material and ore stockpiles; solid tailings remaining after leaching of the ore; and liquid effluents arising from purification and subsequent chemical operations. Tsivoglou & O'Connell [1962] surveyed waste treatment methods capable of reducing the environmental impact of uranium mining and milling. This report and an earlier paper [Ryan & Alfredson 1975] summarising many of the results are concerned with the methods required for the treatment of only mine water and liquid effluents arising from the treatment plant, particularly the raffinate or barren liquor which is discharged after the recovery and purification of the uranium from the leach liquor.

Large volumes of water may seep, fall or run off into open-cut mines, especially during periods of heavy rainfall, and must be removed continuously. Depending on the volume of water and composition of the ore (e.g. presence of sulphides), pit water will contain various contaminants and, in the case of ground waters, the concentration of radium will be of particular concern because only very low concentrations are generally acceptable. If a population living near a uranium mill received a radiation dose from only the radium content of its drinking water supply, the maximum permissible concentration (mpc) for radium in the drinking water would be 10 pCi ℓ^{-1} [ICRP 1959]. If, however, other exposure routes were involved, allowable levels may be considerably reduced.

The composition of the raffinate depends on the type of process used (acid or alkaline leaching, purification by ion exchange or solvent extraction). This work is related to acid leaching processes and the raffinate is then acidic and contains soluble chemical reagents, traces of heavy metal impurities, radium and daughter products as well as soluble and entrained organic extraction agents (e.g. the tertiary amine, Alamine-336). The composition of all the raffinate and pit water samples used in this experimental study is given in Table 1.

In general, depending on environmental considerations, effluent streams may be disposed of, with or without treatment, by discharge with associated dilution to rivers or streams, by evaporation from tailings dams or ponds, or by deep well injection [Beverly 1968; Tsivoglou & O'Connell 1963; Whitman & Porter 1958]. In addition the extent to which the effluents must be decontaminated is related to the environment in which their discharge or storage may occur. Thus, one of the aims of the Northern Territory Uranium Province Environmental Program [Davy, Giles & Conway 1973] was to establish levels of discharge of contaminants acceptable to that environment. It appears that the principal contaminants of concern in the raffinates in Table 1 are radium, free acid, dissolved salts, uranium, copper, lead, zinc and organic reagents, e.g. amine. Even if retention of effluents in tailings and other dams is carried out, treatment to remove pollutants to acceptable levels may still be required because of possible seepage to ground waters, accidental overflow or structural failure.

2. PREVIOUS WORK ON TREATMENT OF LIQUID WASTES

2.1 Neutralisation and Precipitation

Neutralisation of acid raffinates as a method of waste treatment is normal practice in many metallurgical processes [Blesing & McMahon 1973; Straub 1964]. Whitman & Porter [1958] reported that most components in waste solutions from uranium mills could be reduced to acceptable concentrations by neutralisation to pH 10. For example, iron, copper and uranium are removed below pH 7.5, but only 40 per cent of sulphate and practically no nitrate are removed at pH 10. Up to a 90 per cent reduction in radium concentrations has also been observed at a pH of 7.0 [Tsivoglou & O'Connell 1963]. The choice of pH is based on economics and process efficiency at each site. Economically, it is desirable to use the lowest pH (i.e. least amount of neutralising agent) which will achieve the required pollutant concentrations. A further limit on the choice of pH can arise from the requirement of waste disposal authorities in Australia that waste water be neutralised to a pH between 6.5 and 9.8, depending on the method of disposal [Palmer 1972]. The commonest neutralising agents are lime and limestone.

Many workers have investigated neutralisation and precipitation for the removal of calcium and radioactive strontium, which have similar chemical properties to those of radium, from aqueous wastes generated at nuclear laboratories. The use of lime-soda ash mixtures for neutralisation was investigated by Cowser *et al.* [1965] who found that the efficiency was improved by the addition of coagulants. Burns *et al.* [1965] found that precipitation with calcium-iron phosphate successfully removed strontium as a major contaminant, but if calcium was present in significant quantities, precipitation with calcium phosphate-copper ferrocyanide was preferred. Neutralisation with caustic soda gave decontamination factors approaching 10 for strontium [Holcomb 1963] and with lime a factor of 20 was obtained for radium [Feldman 1961].

Clarification in the neutralisation process may be promoted by the precipitation of aluminium hydroxide, calcium phosphate-ferrous sulphate or copper ferrocyanide [Sugimoto & Ishihara 1965] and can be efficiently carried out in a sludge blanket [Burns *et al.* 1965; Blanco *et al.* 1965] or fluidised bed. Control of zeta potential to ± 3 mV has also been demonstrated to improve clarification [Blanco *et al.* 1965; Yee, Delora & Shockley 1970].

2.2 Removal of Radium

Co-precipitation of radium with a barium salt (usually barium chloride) is used for radium removal from neutralised effluent streams in the United States [Beverly 1968] and Canada [Yourt 1966]. Typically, 50 to 300 mg Ba ℓ^{-1} of solution is added depending on the characteristics of the effluent. Feldman [1961] reported that 0.03 M sulphate was required to give good radium removal and that the efficiency was decreased when the mole ratio of barium to sulphate exceeded 0.25.

The removal of radium by adsorption on barytes has also been investigated [USAEC 1960; Arnold & Crouse 1965]. More than 90 per cent of the radium in uranium mill effluent was adsorbed on -100 + 150 mesh barytes in the pH range 1 to 12 when the sulphate concentration was > 0.03 M. For a given contact time, the radium absorbed varied inversely with the particle size. Arnold & Crouse [1965] also investigated the use of natural and synthetic zeolites for radium removal. In packed column tests with a radium feed concentration of 2300 pCi ℓ^{-1}, they found that the residual radium content was maintained at < 10 pCi ℓ^{-1} for up to 3000 volumes of liquid passed through the bed for barytes, 2600 bed volumes for Decalso and 480 bed volumes for clinoptilolite. Similar studies of the use of vermiculite for strontium removal have been reported by Burns *et al.* [1965]. Recently Moore & Cook [1975] reported that acrylic fibres impregnated with oxides of manganese were effective in reducing radium levels in contaminated wells to within drinking water limits.

2.3 Removal of Organic Materials

Partial recovery of the entrained organic phase from raffinates and slurries by scrubbing with kerosene in packed beds [Alfredson *et al.* 1974], pulsed columns [Ritcey, Slater & Lucas 1973] and spray columns [Kumar 1973] has been reported on the pilot plant scale. Removal of organic material by adsorption on solids during neutralisation has also been reported to be effective [Palmer 1972].

Two methods for the further removal of organic constituents from waste streams, which may be applicable to the treatment of uranium mill effluents, are absorption on granulated beds of activated charcoal [Palmer 1972] and treatment by various oxidation processes [Roberts 1973].

2.4 New Separation Techniques

Foam separation and reverse osmosis are potential methods for water renovation involving the removal of soluble salts and organic materials from waste solutions containing 500 - 10,000 mg ℓ^{-1} dissolved solids. Davis, Kibbey & Schonfeld [1965] described a foam separation process for the decontamination of process waste water containing strontium and other radionuclides. Wace & Banfield [1966] and a number of other workers [Lemlich 1972] have outlined the theory of foam separation and noted several possible applications, including the removal of large organic molecules from aqueous solutions.

Although reverse osmosis has been developed for the production of potable water from brackish feeds, there is still scope for the development of improved membranes capable of treating feed solution which has a higher salt content. Palmer [1972] pointed out the usefulness of this method for removing dissolved ions, organic molecules, etc. Other membrane processes and hyperfiltration may also be applicable to the removal of organic pollutants from waste solutions.

3. SCOPE OF STUDY

The complex nature of uranium ores means that effluents from different plants will vary considerably and treatment methods for each waste stream will need to be investigated to ensure that adequate decontamination can be achieved. In this study, a selection of effluent samples was treated by conventional processes designed to reduce contaminant levels. The following treatment methods were studied on a laboratory scale:

- single stage neutralisation of acid raffinates using lime, lime-soda ash mixtures, caustic soda and limestone;
- two-stage neutralisation of raffinates using limestone in the first stage and lime in the second stage;
- scrubbing of raffinates with odourless kerosene to recover Alamine-336;
- addition of barium chloride to neutralised raffinate to reduce radium concentration by co-precipitation of barium and radium sulphates;
- conditioning of pit water with sulphates followed by barium chloride treatment to remove radium; and
- removal of radium from raffinates and pit water by adsorption on barytes.

4. EXPERIMENTAL EQUIPMENT AND PROCEDURE

Laboratory scale batch neutralisation tests using lime, lime-soda ash mixtures, caustic soda and limestone were carried out in 0.4 and 2 ℓ glass beakers stirred with stainless steel centrifugal impellers at 15 s^{-1}. The beakers were half-filled with acid raffinate and varying amounts of neutralising agent were added over 30 or 60 minutes. The pH of the slurry was measured at frequent intervals, using a pH meter with a glass electrode, or continuously recorded on a Honeywell-Brown millivolt recorder. After the neutralisation period, the slurry was filtered immediately through a Buchner funnel (Whatman No.1 filter paper) and samples of the filtrate were taken for analysis.

Continuous neutralisation tests were carried out using an 0.4 ℓ glass beaker as the reactor. Raffinate was pumped to the neutralisation vessel and the pH was measured and kept constant by controlling the rate of addition of lime. The neutralised raffinate was withdrawn from the vessel, filtered, sampled and analysed.

Laboratory scale batch tests of co-precipitation of radium and barium sulphates with barium chloride were carried out in a similar manner. Barium chloride was added as 100 g Ba ℓ^{-1} solution to give the required concentration. In general, all samples for radium analysis were filtered (Whatman No.542 filter paper) and acidified with 2 cm^3 of

16 M nitric acid per 100 cm^3 of sample to prevent adsorption of radium on the surfaces of the glass sample bottle.

Batch tests and a column experiment were carried out to investigate radium removal from raffinates and pit water by adsorption on barytes. In the batch tests, 8 g samples of barytes were mixed with 200 cm^3 of raffinate as in the neutralisation experiments. In the column test, neutralised raffinate was metered at 0.18 $\ell\ h^{-1}$ to a glass column (9 mm i.d.) packed with 16 g barytes (in the size range -14 +18 BSS) to a height of 91 mm, giving a bed volume of 5.8 cm^3. The flowrate was checked every hour and radium analyses were made on half-hourly composite samples.

Raffinates and mine waters were analysed for radium by co-precipitation with lead sulphate followed by dissolution in EDTA and co-precipitation with barium sulphate [Lovell, Morgan & Palmer 1961]. The alpha activity was determined in a low background gas flow proportional counter. Results were reported on the basis that all radium was present as ^{226}Ra.

The recovery of amine from raffinates was also examined in batch and column experiments. In the former, 20 cm^3 samples of raffinate were mixed for 20 minutes with various volumes of odourless kerosene (Shellsol T) in glass beakers equipped with stainless steel stirrers operating at 14 s^{-1} to give organic/aqueous ratios ranging from 1:2 to 24:1. The two phases were allowed to separate and the aqueous phase was then removed by pipetting, centrifuged for 10 minutes to remove entrained organic droplets, and sampled for amine analysis. In the column experiments, 13 ℓ of odourless kerosene was continuously recycled through a glass column (45 mm diameter) packed with 6 mm stainless steel Raschig rings to a height of 0.4 or 1.0 m, and containing 0.5 ℓ of raffinate. Average kerosene flowrates of 1.4 to 16 $\ell\ h^{-1}$ were used. The raffinate was sampled intermittently and analysed for amine.

5. RESULTS AND DISCUSSION

5.1 Neutralisation of Raffinates

5.1.1 Single stage neutralisation

Neutralisation curves are shown in Figure 1 as plots of pH against the cumulative mass of reagent added at 3 minute intervals. The quantity of reagent added was varied to give approximately equal changes in pH with each addition; typically, twenty additions were required to span the complete pH range. The curves indicate differences in neutralisation with lime, limestone, lime-soda ash mixtures and caustic soda. Although the first two materials are the least expensive, the others were investigated to see if they were more effective than lime in the removal of radium and heavy metal impurities. With lime and caustic soda, two distinct inflections were observed between pH 4 and 9 and between pH 9 and 12, whereas the curves for lime-soda ash mixtures show only one inflection in the lower pH range followed by a slow increase in pH. The amount of lime required to attain a given pH was a function of the initial pH and composition of the raffinate (Figure 2). For example, the lime required to attain a pH of 8 varied from 4.3 kg m^{-3} for raffinate C to 25 kg m^{-3} for raffinates B and C. The low lime requirement for raffinate C was due to the lower acid consumption in leaching and the consequent reduction in the amount of gangue materials dissolved with the uranium.

When limestone was used to neutralise raffinates, its particle size had a considerable effect on the rate and extent of the neutralisation reaction. Figure 3 shows that, to attain a pH of 4 or greater, limestone with an average particle size of < 100 μm was required, and to reach a pH of from 5 to 6 an average particle size of < 50 μm was necessary. For a given mixing time, pH increased with the amount of limestone until a plateau was reached. For a given addition of limestone, pH increased with reaction time (Figure 4). Comparison of the neutralisation curves for lime and limestone indicates that the performance of limestone is superior to that of lime below pH 4.5.

Samples of raffinates neutralised to various values of pH with lime, limestone and lime-soda ash mixtures were analysed in detail to investigate the effect of the reagent and pH on the concentration of pollutants (Tables 2-4). Batch experiments with lime demonstrated that there was no significant reduction in the concentrations of iron, phosphorus, copper and lead above pH 7. However, a pH of up to 10 was required before there was no further removal of dissolved solids, uranium and zinc. Sulphate concentration decreased as the pH increased but chloride concentration was little affected.

Two tests of continuous neutralisation with lime to pH 7 were carried out. The results shown in Table 5 indicate a slight improvement in heavy metal removal in the continuous experiments compared with batch neutralisation, but increasing the retention time from one to fifty minutes had little effect on contaminant levels.

Batch tests established that lime-soda ash mixtures were less effective in removing heavy metals than lime alone (compare Tables 2 and 3). Uranium and lead were removed satisfactorily but the removal of copper and zinc was relatively poor. The total dissolved solids remained quite high, due largely to the presence of sodium in solution.

Neutralisation with limestone was quite effective in removing copper, lead, uranium and Alamine-336 from solution. The difficulty of achieving a pH above 4.5, as demonstrated in Figure 3, however limits its use to primary treatment in a two-stage neutralisation process.

5.1.2 Two-stage neutralisation

Comparison of the neutralisation curves for limestone and lime in Figure 1 indicates that the performance of limestone is superior at low values of pH and that two-stage precipitation using limestone in the first stage and lime in the second may be advantageous. The optimum pH for the first stage appears to be about four. Samples of raffinate adjusted to pH 4 with limestone then neutralised to pH values from 7 to 11.6 with lime, produced clarified liquors generally similar in composition to those obtained using lime neutralisation alone (compare Tables 6 and 2). As with lime neutralisation, increasing the final pH decreased the concentration of contaminants in the clarified liquor. Table 7 shows that limestone particle size had little effect on the composition of neutralised raffinate. The coarser limestone particles, however, required a longer reaction time to reach pH 4 in the first stage.

The effect of first-stage pH on liquor composition is shown in Table 8. As expected, the concentration of contaminants in the clarified liquor from the first stage decreased with increasing pH. The concentration of copper, zinc and uranium decreased sharply between pH 3 and 6. Finely ground limestone and long residence times, both of which are economically undesirable, must be used to reach the higher values of pH in the first stage.

5.1.3 Discussion

The neutralisation curve for a raffinate can be predicted using solubility product data if the concentration and form (e.g. Fe^{2+} or Fe^{3+}) of the major components of the raffinate are known. Figure 5 shows such a curve calculated for raffinate C assuming the major metal ions (Al^{3+}, Fe^{3+}, Mg^{2+} and Mn^{2+}) are precipitated as hydroxides while silicon and phosphorus are precipitated as calcium silicate and calcium hydrogen phosphate. Although there is some uncertainty as to the actual species precipitated (e.g. some basic carbonates or sulphates may be formed), these assumptions are useful in providing a first-order estimate of lime consumption. The agreement between theoretical and experimental curves for raffinate C is considered satisfactory, particularly as the precise form of the iron, silicon and phosphorus is unknown. Theoretical calculations indicate that the bulk of the iron and aluminium is precipitated before pH 4. Between pH 4 and 8, silica, phosphate and copper are precipitated and the lime consumption is small. In stronger alkaline solutions, manganese and magnesium are precipitated and some aluminium hydroxide dissolves forming aluminates.

The concentrations of some of the minor constituents in neutralised raffinate are also important because of their effect on the biosystem. Neutralised raffinate is not generally discharged to the environment but seepage from tailings dams can result in release. Table 9 lists the drinking water standards of several countries [Hart 1974]. Comparison of Table 9 and Tables 2-8 indicates that most raffinates neutralised to pH 7 or greater contain heavy metals at concentrations below the maximum levels for drinking water. Lead concentrations, however, often exceed the standards.

The drinking water standard for humans is, of course, not the only basis for assessment of environmental impact. Other life forms, particularly aquatic species, may concentrate pollutants or may be more vulnerable to certain trace metals. For example, the 96-hour median tolerance limits (TLm_{96}) for hardyheads (*Cratercocephalus marjorial*), an abundant fish in the uranium province of the Northern Territory, are 0.04, 0.18 and 0.14 mg ℓ^{-1} for copper, lead and zinc, respectively [Giles 1974]. Hart [1974] recommended applying factors of 0.05, 0.01 and 0.005 respectively to these TLm_{96} values in order to obtain derived working levels. This leads to extremely low concentrations for these heavy metals, though there is evidence [Giles 1974] that increases in the hardness of the receiving water can produce synergistic effects that reduce toxicity. Reducing heavy metal concentrations below the derived working levels could pose such technical and economic challenges that, in practice, impoundment of neutralised raffinate streams may be preferable.

The effects of pH on the theoretical solubility curves for copper, lead and zinc have been calculated from solubility product data [Argaman & Weddle 1974]. Figures 6-8 show these curves along with experimental data. The amphoteric behaviour of lead and zinc at high pH is also shown [Orion Research 1972]. The tendency towards lower metal concentrations compared with theoretical values may be partially explained by adsorption of ions on the surface of precipitated particles or formation of less soluble species. For example, copper may be precipitated as the basic carbonate, malachite ($Cu_2(OH)_2CO_3$), rather than the hydroxide.

5.2 Removal of Radium

The radium concentration in raffinates decreased with increasing pH during lime neutralisation but there was considerable scatter in the experimental data (Figure 9). Various attempts were made to improve the reproducibility of these results without any significant success. This problem has been reported often [Arnold & Crouse 1965; Beverly 1968; USAEC 1960; Feldman 1961]. A number of factors of suggested importance include the possibility of radium being associated with fine particles which are not filtered out or reproducibly sampled, and of radium being adsorbed on the walls of the container, especially under alkaline conditions.

Neutralisation with lime in the pH range 7 to 8.5 generally reduced the radium concentration to between 10 and 200 pCi ℓ^{-1}. Lime-soda ash mixtures appeared to give better removal of radium than lime alone (Table 3) but the residual concentration was still high enough to require further treatment. Two-stage neutralisation was also more effective than single stage lime neutralisation, provided the solids precipitated at the limestone stage were not removed before lime addition (Table 6). It appears that these solids removed radium by surface adsorption.

Additional treatment of neutralised raffinates is generally required to reduce the radium concentration to acceptable levels. Coprecipitation of barium and radium sulphate by the addition of barium chloride ($BaCl_2$) or adsorption on barytes was shown to be effective. The addition of as little as 10 mg Ba ℓ^{-1} raffinate reduced the radium concentration of neutralised raffinates (pH in the range 7 to 10) from initial values ranging from 9 to 38 pCi ℓ^{-1}, to less than 3 pCi ℓ^{-1}. Radium removal was not improved by adding up to 500 mg Ba ℓ^{-1} raffinate.

In batch absorption tests using barytes, low residual radium concentrations were obtained in all but one experiment with raffinates neutralised to a pH in the range 9.6 to 9.9 (Table 10). However, the removal of radium from raffinate, which was only partly neutralised (pH 3.5), was much less effective. No significant effect of particle size on residual radium concentration was observed in these tests. In a single column experiment, the radium concentration was reduced from an inlet concentration of 7 pCi ℓ^{-1} to 1 pCi ℓ^{-1} throughout the duration of the test in which 1080 bed volumes of raffinate were treated.

5.3 Removal of Amine

Although the solubility of Alamine-336 in raffinates is reported to be approximately 4 mg ℓ^{-1} [Bellingham 1960], considerably higher concentrations are observed in practice, and make-up for amine losses constitutes a significant operating cost. The amine content of the raffinates in Table 1 varies from 5 to 31 mg ℓ^{-1} suggesting that most is present as an entrained organic phase. However, centrifuging a sample of raffinate B at 530 times gravity had no effect in reducing the amine content.

Partial recovery of amine from raffinate by extraction with kerosene before neutralisation was investigated in both batch equilibration experiments and continuous differential extraction tests in a packed column. In the batch tests (Table 11), amine concentration was reduced by an average of 40 per cent. The results of the column experiments which were generally consistent with these data, indicated that the amine concentration in the raffinate could not be reduced below ~ 8 mg ℓ^{-1} by this method. Extraction with kerosene does not appear to be an effective means of reducing amine concentrations to low levels.

While recovery of amine proved to be impracticable, its concentration was reduced during neutralisation with lime, limestone and lime-soda ash mixtures (see Tables 2-4). In general, the percentage removal of amine increased with increasing pH and the amount of solids precipitated which provided surface for adsorption. The residual amine in solution was substantially higher for raffinate C than for A because of the higher initial concentration and the smaller quantity of precipitated solids.

If neutralised raffinate is discharged to a tailings dam, any tendency for amine to be released from the precipitated solids on standing, or in the event of a large influx of water into the dam during heavy rainfall, would be undesirable. A quantity of raffinate B was neutralised to pH 7 and two samples of slurry were taken and filtered. The residue from one sample was re-pulped with neutralised raffinate while the other residue was contacted with demineralised water (simulating dilution with rainwater). Liquid samples were periodically withdrawn. The results, shown in Table 12, indicated that 5 to 10 per cent of the amine was released initially but was re-adsorbed within one month.

The possibility that the presence of amine as a surface film would inhibit evaporation from a tailings dam was investigated using several samples of raffinates and synthetic mixtures. The samples were contained in measuring cylinders and located outside the laboratory so that the evaporation conditions for each sample were similar. The results which are shown in Figure 10 indicated that evaporation is not adversely affected by the presence of amine.

5.4 Treatment of Pit Water

The addition of lime to pit water showed little evidence of precipitation, which is consistent with the very low concentration of dissolved solids, and cannot therefore provide any significant removal of radium.

The efficiency of removal of radium from pit water by co-precipitation of barium and radium sulphate was investigated in terms of the amount of barium chloride and sulphate which was added. Feldman [1961] previously reported the need for a minimum of 0.03 M sulphate for efficient removal. In this work, the addition of 0.001 to 0.05 M sulphate as sulphuric acid, or sodium, ammonium or calcium sulphate was examined. Figure 11 shows that the amount of barium chloride had little effect on the residual radium concentration in the range 10 to 500 mg Ba ℓ^{-1} raffinate containing 0.03 M ammonium or sodium sulphate. However radium removal from acidic solution was much less efficient, which is consistent with the results for radium removal from neutralised raffinates. When 20 mg Ba ℓ^{-1} raffinate was used, the addition of approximately 0.01 M ammonium, calcium or sodium sulphate was sufficient to reduce the radium concentration to < 3 pCi ℓ^{-1}. As shown in Figure 12, even less ammonium or sodium sulphate (0.005 M) would probably be adequate.

In batch tests of radium removal by adsorption on barytes, the residual radium concentration was reduced from 140 to 2 pCi ℓ^{-1} by the addition of 0.03 M sodium sulphate at pH 8.4, whereas with pit water (pH 8.3) the concentration was reduced from 150 to 22 pCi ℓ^{-1}. Poor radium removal was obtained under acidic conditions; at pH 1.9 radium concentration fell from 376 to 148 pCi ℓ^{-1}.

6. CONCLUSIONS

Neutralisation with lime is a simple, cheap and effective means of treating acid raffinates from uranium processing to raise the pH, reduce the concentrations of dissolved salts including heavy metal impurities and remove amine by adsorption. The efficiency of removal is a function of pH; at pH 7 there were only very low concentrations of iron, phosphorus, copper and lead remaining, but neutralisation to pH 10 was required for best removal of dissolved salts, uranium, zinc and amine. Limestone was more efficient than lime for neutralisation at < pH 4.5 and two-stage precipitation using limestone in the first stage at approximately pH 4 and lime in the second, without interstage separation of solids, may be advantageous.

The concentration of residual amine in raffinate after neutralisation was a function of the initial concentration and the amount of solids precipitated which provided surface for adsorption. Tests simulating likely conditions in a tailings dam indicated that there is no long-term tendency for the amine to be released. The presence of amine was also shown not to affect the rate of evaporation of raffinate. Attempts to recover amine from raffinate before neutralisation by contacting with kerosene did not reduce the amine concentration below 8 mg ℓ^{-1}.

Lime neutralisation of raffinates in the pH range 7 to 8.5 generally reduced the radium concentration to 10-200 pCi ℓ^{-1}, but there was considerable scatter in the experimental data. The range of radium concentration was readily reduced to < 3 pCi ℓ^{-1} by co-precipitation of barium and radium sulphate with the addition of 10 mg Ba (as $BaCl_2$) ℓ^{-1} raffinate and was not reduced further by adding up to 500 mg ℓ^{-1}. Adsorption of radium on barytes was also effective in reducing the radium concentration in neutralised raffinates to < 3 pCi ℓ^{-1} in both batch and column experiments.

Removal of radium from pit water was demonstrated as a function of the amount of barium chloride and sulphate added. With 0.03 M sodium sulphate, the addition of 10 mg Ba ℓ^{-1} was sufficient to reduce the radium concentration from 140 to < 3 pCi ℓ^{-1}. When 20 mg Ba ℓ^{-1} was used, 0.01 M sulphate as ammonium, calcium or sodium sulphate was sufficient for efficient removal of radium. Adsorption on barytes also appears effective for the removal of radium from pit water containing 0.03 M sodium sulphate.

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TABLE 1

COMPOSITION OF RAFFINATES AND PIT WATER

Component	Composition (mg ℓ^{-1})				
	Raffinate A (pH = 1.3)	Raffinate B (pH = 1.7)	Raffinate C (pH = 2.1)	Raffinate D (pH = 1.8)	Pit Water (pH = 8.2)
TDS*	58,400	45,300	21,200	50,000	140
Al	n.a.†	n.a.	500	1,840	2
As	n.a.	n.a.	<0.07	<0.5	<0.07
Ba	n.a.	n.a.	<0.05	<0.05	<0.05
Ca	29	32	25	150	4
Cu	43	73	15	80	<0.04
Fe	2,690	2,230	340	2,300	<0.15
Hg	n.a.	n.a.	0.007	n.a.	0.003
Mg	1,940	1,880	800	1,880	34
Mn	870	730	300	7	<0.1
Ni	10	10	5	12	<0.07
Pb	2.7	1.9	0.5	1.2	<0.005
Si	440	390	104	430	11.0
U	1.3	0.7	86	2.8	0.07
V	17	24	3	16	<0.04
Zn	17	8	2	7	<0.04
Cl	1,540	580	200	360	8.2
P	300	290	410	280	<0.05
NO_3	n.a.	n.a.	n.a.	n.a.	19
SO_4	35,400	27,100	6,000	26,300	67
Amine	4.8	10.7	31	9.7	n.a.
Ra (pCi ℓ^{-1})	26,000	15,000	2,400	790	140

* *TDS Total dissolved solids*

† *n.a. not available*

TABLE 2

NEUTRALISATION OF RAFFINATES WITH LIME

Raffinate	pH	Composition (mg ℓ^{-1})																Ra
		TDS*	Ca	Cu	Fe	Hg	Mg	Mn	Ni	Pb	Si	U	V	Zn	Cl	P	SO_4	Amine	(pCi ℓ^{-1})
A	4.3	27,000	-	27	-	-	-	-	-	0.7	-	0.45	-	16.0	-	-	-	4.2	2,400
	8.7	15,700	-	0.05	-	-	-	-	-	<0.4	-	<0.005	-	<0.03	-	-	-	0.32	37
	9.6	6,100	67	<0.05	<0.5	-	5.5	<0.05	<0.1	<0.5	0.3	<0.005	<0.6	0.05	1,460	<1.0	1,840	<0.05	610
	11.6	6,100	-	0.08	-	-	-	-	-	<0.4	-	<0.005	-	<0.05	-	-	-	<0.05	120
	12.0	6,450	-	0.05	-	-	-	-	-	<0.4	-	<0.005	-	<0.03	-	-	-	<0.05	45
B	3.9	20,900	-	65	-	-	-	-	-	0.6	-	1.7	-	7.0	-	-	-	1.2	-
	5.2	21,600	-	6.6	-	-	-	-	-	0.7	-	2.6	-	5.5	-	-	-	12.4	-
	6.4	11,600	-	2.0	-	-	-	-	-	0.4	-	1.1	-	1.1	-	-	-	1.9	-
	7.0†	-	-	<0.03	-	-	-	-	-	0.002	-	0.021	-	0.025	-	-	-	<0.1	8
	7.4	19,400	-	0.1	-	-	-	-	-	0.4	-	0.26	-	0.2	-	-	-	0.7	-
	8.1	14,700	-	0.1	-	-	-	-	-	0.3	-	0.47	-	0.3	-	-	-	2.9	-
	8.5	6,840	-	0.05	-	-	-	-	-	0.3	-	0.28	-	0.05	-	-	-	0.3	-
	11.6	4,760	-	0.05	-	-	-	-	-	0.3	-	0.36	-	0.05	-	-	-	0.5	-
	11.9	4,160	-	0.05	-	-	-	-	-	<0.3	-	0.015	-	0.02	-	-	-	<0.02	-
	12.1	4,320	-	0.05	-	-	-	-	-	<0.03	-	0.090	-	0.01	-	-	-	<0.02	-
C#	6.3	9,600	530	<0.03	<0.2	7	560	270	5.0	0.02	6.8	0.11	<0.8	0.23	207	0.5	5,800	12.8	400
	7.3	9,600	480	<0.03	<0.2	<3	520	220	<0.1	0.02	1.3	0.02	<0.8	<0.04	201	<0.5	5,100	2.8	82
	7.7	7,900	510	<0.03	<0.2	<3	470	120	<0.1	0.02	0.29	0.38	<0.8	<0.04	187	<0.5	4,800	3.9	70
	8.4	8,000	440	<0.03	<0.2	<3	510	47	<0.1	0.02	0.41	3.6	<0.8	<0.04	221	<0.5	4,700	0.84	34
	8.8	7,300	480	<0.03	<0.2	8	440	18	0.7	0.02	0.35	1.3	<0.8	<0.04	243	<0.5	4,100	1.4	43
D	4.0	36,500	-	69	137	-	-	-	-	0.7	51.6	2.8	-	7.7	-	29.3	19,700	3.7	380
	6.0	24,600	-	0.18	<0.2	-	-	-	-	0.4	1.8	<0.008	-	0.26	-	<0.6	12,000	1.7	18
	7.0	18,000	-	0.06	<0.2	-	-	-	-	0.4	0.4	0.0032	-	0.05	-	2.0	10,900	<0.2	300
	8.2	19,100	-	<0.02	<0.2	-	-	-	-	0.3	<0.5	<0.003	-	<0.25	-	<0.6	9,150	0.3	69
	10.0	3,950	-	<0.02	<0.2	-	-	-	-	0.4	<0.5	0.007	-	<0.025	-	<0.6	2,080	<0.1	5
	12.4	4,600	-	0.02	<0.2	-	-	-	-	0.15	0.1	<0.002	-	0.02	-	<0.01	1,580	<0.2	10

* *Total dissolved solids*

† *Continuous neutralisation experiment*

Neutralised solution was also analysed for arsenic and barium. The concentrations of these elements were below the limits of detection; As < 0.1 mg ℓ^{-1}, *Ba < 0.05 mg* ℓ^{-1}.

TABLE 3

NEUTRALISATION OF RAFFINATE A WITH LIME-SODA ASH MIXTURES

$Ca(OH)_2/Na_2CO_3$ (molar ratio)	pH	Concentration in Solution (mg ℓ^{-1})						Ra (pCi ℓ^{-1})
		TDS$^+$	Cu	Pb	U	Zn	Amine	
-	1.3	58,400	43.0	3.0	0.96	19.0	5.5	26,000
1.0	10.0	36,800	0.7	<0.4	<.005	0.14	<0.05	21
1.25	10.25	31,700	3.4	0.6	<.005	0.13	<0.05	6
1.5	10.0	26,000	0.2	<0.4	<.005	0.12	0.70	17
1.75	10.2	24,500	0.2	<0.4	<.005	0.13	<0.05	4
2.0	10.2	22,000	0.2	<0.4	<.005	0.10	<0.05	7

+ TDS Total dissolved solids

TABLE 4

NEUTRALISATION OF RAFFINATE B WITH LIMESTONE

(limestone particle size; -240 BSS)

pH	Composition (mg ℓ^{-1})					
	Ca	Cu	Pb	U	Zn	Amine
4.4	410	61	0.5	1.4	12	1.8
5.5	425	4.1	0.5	0.018	8.9	1.6
6.1	445	0.1	0.5	0.0084	1.6	<0.02
6.4	450	0.1	0.5	0.0072	0.8	<0.02
6.5	490	0.1	0.5	0.018	0.7	<0.02

TABLE 5

CONTINUOUS NEUTRALISATION OF RAFFINATE B WITH LIME AT pH 7

Average Residence Time (min)	Hours after start	Concentration in solution (mg ℓ^{-1})					Ra (pCi ℓ^{-1})
		Cu	Pb	U	Zn	Amine	
1.14	50.4	<0.008	0.05	0.004	<0.005	<0.2	5
	59.7	<0.008	0.06	<0.004	<0.005	<0.2	15
	80.2	0.035	<0.03	0.005	0.020	0.5	9
50.5	32	0.07	0.2	0.023	0.1	2.2	7
	80	2.6	0.14	0.024	0.71	4.1	21
	120	0.055	0.004	0.015	0.025	<0.1	8
	128	<0.03	0.002	0.021	0.025	<0.1	8
	136	0.055	<0.002	0.022	0.036	<0.1	12
	144	0.03	0.006	0.018	<0.015	<0.1	7

TABLE 6

TWO-STAGE LIMESTONE-LIME NEUTRALISATION OF RAFFINATES

(limestone particle size < 64 μm)

Sample	pH	Concentration in solution (mg ℓ^{-1})					Ra (pCi ℓ^{-1})
		Cu	Pb	U	Zn	Amine	
RAFFINATE B							
2nd stage filtered	7	0.09	<0.04	0.03	0.23	0.7	140
2nd stage unfiltered	7	0.03	<0.04	0.03	0.03	<0.2	24
RAFFINATE D - RUN 1							
1st stage	4	77	0.6	3.0	10.0	3.4	620
2nd stage filtered	7	0.25	0.4	0.07	0.07	0.9	170
2nd stage unfiltered	7	0.25	0.4	0.11	0.08	0.6	20
RAFFINATE D - RUN 2							
1st stage	4	73	0.6	2.9	10.8	4.7	860
2nd stage filtered	7	0.39	0.4	0.05	0.06	0.9	110
2nd stage unfiltered	7	0.12	0.4	0.11	0.05	1.0	24
RAFFINATE D - RUN 3							
1st stage	4	72	0.6	2.2	10.0	3.8	730
2nd stage filtered	10	-	-	0.005	-	0.19	50
2nd stage unfiltered	10	0.02	0.03	0.001	<0.005	0.09	6
RAFFINATE D - RUN 4							
1st stage	4	66	0.6	5.6	9.4	4.3	430
2nd stage filtered	10	0.03	0.03	0.004	<0.005	0.10	50
2nd stage unfiltered	10	0.02	0.06	0.006	<0.005	0.10	5
RAFFINATE D - RUN 5							
1st stage	3.9	70	0.4	4.1	10.5	0.87	460
2nd stage filtered	7.6	0.06	0.4	0.03	0.11	<0.2	34
2nd stage unfiltered	7.1	0.18	0.3	0.03	0.10	2.5	5
RAFFINATE D - RUN 6							
1st stage	4	70	0.3	3.9	12.5	2.8	530
2nd stage filtered	8.3	0.04	0.4	0.01	0.05	<0.2	28
2nd stage unfiltered	8.4	<0.015	0.3	0.01	<0.01	<0.2	6
RAFFINATE D - RUN 7							
1st stage	4	-	-	-	-	-	390
2nd stage filtered	10.2	<0.015	<0.2	0.002	<0.01	<0.2	50
2nd stage unfiltered	9.8	<0.015	<0.2	0.009	<0.01	<0.2	6
RAFFINATE D - RUN 8							
1st stage	4	70	0.4	47	8.7	4.0	360
2nd stage filtered	11.6	-	-	0.1	-	-	14
2nd stage unfiltered	11.6	<0.015	<0.2	<0.001	<0.01	<0.2	4

TABLE 7

EFFECT OF LIMESTONE PARTICLE SIZE ON TWO-STAGE NEUTRALISATION OF RAFFINATE D

Sample	Average Particle Size (µm)	Run No.	pH	Concentration in solution (mg ℓ^{-1})					Ra (pCi ℓ^{-1})
				Cu	Pb	U	Zn	Amine	
Solution from first stage	1,204	1	4	71	0.6	0.7	8.6	2.5	530
	1,204	2	4	70	0.35	2.6	14.0	1.5	350
	324	3	4	72	0.4	4.1	8.2	6.2	850
	231	4	4	68	0.35	3.4	7.9	2.4	1,270
	<211	5	4	73	0.8	2.6	8.6	5.9	270
	138	6	4	64	0.25	2.4	12.5	2.5	190
	<64	7	4	77	0.6	3.0	10.0	3.4	620
	<64	8	4	73	0.6	2.9	10.8	4.7	860
Solution from second stage - no interstage filtration	1,204	1	7	0.02	0.4	0.03	0.04	0.4	310
	1,204	2	6.8	0.23	0.4	-	0.2	-	65
	324	3	7.0	0.12	0.35	<0.002	0.14	0.5	-
	231	4	7.0	0.07	0.3	0.02	0.09	0.4	51
	<211	5	7.0	<0.02	<0.3	0.02	0.04	0.6	2
	138	6	7.3	0.05	0.25	0.05	0.01	0.3	51
	<64	7	7.0	0.25	0.4	0.11	0.08	0.6	19
	<64	8	7.0	0.12	0.4	0.11	0.05	1.0	24
Solution from second stage - interstage filtration	1,204	1	7	<0.02	0.7	0.03	0.04	0.2	130
	1,204	2	6.8	0.14	0.15	0.04	0.07	0.5	180
	324	3	7.0	0.15	0.30	<0.001	0.10	0.4	-
	231	4	7.0	0.04	0.25	0.03	0.06	0.4	80
	<211	5	7.0	<0.02	0.5	0.01	<0.025	0.6	18
	138	6	7.0	0.03	0.25	0.19	0.02	0.2	138
	<64	7	7.0	0.25	0.4	0.07	0.07	0.9	170
	<64	8	7.0	0.39	0.4	0.05	0.06	0.9	110

TABLE 8

EFFECT OF pH OF FIRST STAGE ON TWO-STAGE NEUTRALISATION OF RAFFINATE D

Sample	Average Particle Size (μm)	Run No.	pH	Concentration in solution (mg ℓ$^{-1}$)					Ra pCi ℓ$^{-1}$
				Cu	Pb	U	Zn	Amine	
	<64	1	2.5	70	0.8	4.2	8.5	5.3	1,100
Solution from	<64	2	3.0	72	0.4	3.9	8.1	6.5	2,200
first stage	<64	3	3.5	69	0.4	3.9	11.0	1.5	580
	<53	4	6.3	0.04	0.2	0.05	0.88	<0.2	170
Solution from	<64	1	6.9	0.10	0.35	0.02	0.05	<0.4	4
second stage -	<64	2	7.0	0.16	0.30	<0.002	0.19	<0.4	6
no interstage	<64	3	8.5	0.06	<0.2	0.006	<0.01	0.3	11
filtration	<53	4	9.8	0.02	<0.2	0.011	<0.01	<0.2	8
Solution from	<64	1	7.3	0.11	0.25	0.002	0.09	0.5	23
second stage -	<64	2	7.0	0.08	0.3	0.020	0.03	0.3	8
interstage	<64	3	8.7	0.06	<0.2	0.001	0.03	0.2	47
filtration	<53	4	10.1	0.06	<0.2	0.18	0.03	<0.2	9

TABLE 9

COMPARISON OF DRINKING WATER STANDARDS [Hart 1974]

	Australia Capital Cities (1973)	New South Wales (1972)	U.S.A. (EPA, 1972)	USSR (1970)	WHO International (1971)
pH	7.0-8.5				6.5-9.2
Chemicals (mg ℓ^{-1})					
Arsenic	0.05	0.05	0.1	0.05	0.05
Barium	1.0	1.0	1.0	4.0	
Cadmium	0.01	0.01	0.01	0.01	0.01
Chloride		250	250		200-600
Chromium (Cr^{6+})	0.05	0.05	0.05	0.1	
Copper	0.3-1.0	1.0	1.0	0.1	0.05-1.5
Cyanide	0.01	0.05	0.2	0.1	0.05
Fluoride	1.5	1.5	0.8-1.7	1.5	0.8-1.7
Iron	0.3-1.0	0.3	0.3	0.5	0.1-1.0
Lead	0.05	0.05	0.05	0.1	0.1
Manganese		0.05	0.05		0.05-0.5
Mercury		0.001	0.002	0.005	0.001
Nitrogen (in ammonia)		0.5		2.0	
Nitrogen (in nitrates)	10	10	10	10	10
Selenium	0.01	0.01	0.01	0.001	0.01
Silver	0.05	0.05	0.05		
Sulphate		250	250		200-400
Uranyl ion (UO_2^{2+})		5.0			
Zinc	5.0	5.0	5.0	1.0	5.0-1.5
Radioactivity (pCi ℓ^{-1})					
Radium-226	10		0.5		
Strontium-90	30		5		
Gross α		3			3
Gross β	1,000	30			30

TABLE 10

ADSORPTION OF RADIUM ON BARYTES

Baryte particle size μm	Radium concentration (pCi ℓ^{-1})		
	pH of neutralised raffinate		
	9.9	9.6	3.5*
Neutralised raffinate	9 ± 2	605†	177
1,680-2,057	3 ± 2		36
1,204-1,680	3 ± 2	2	
835-1,204	3 ± 2		46
599-835	3 ± 2	5	
353-599	3 ± 2		19
211-353	4 ± 2	29	

* *Dilution of a sample of raffinate neutralised to pH 3.5.*

† *Result abnormally high.*

TABLE 11

BATCH EXTRACTION OF AMINE FROM RAFFINATES BY KEROSENE

Raffinate	$\frac{\text{Organic}}{\text{Aqueous}}$ (volume ratio)	Temperature (°C)	Initial Amine Concentration (mg ℓ^{-1})	Final Amine Concentration (mg ℓ^{-1})	Extraction Coefficient E_A^o	Amine Extraction (%)
B	0.5	24	9.1	5.1	1.6	44
B	1.0	24	9.1	3.3	1.8	64
B	2.0	24	9.1	4.3	0.58	53
B	4.0	24	9.1	4.4	0.27	52
B	9.0	24	9.1	3.5	0.18	62
B	24.0	24	9.1	3.0	0.08	67
C	1.0	30	35.0	19.4	0.8	45
C*	1.0	30	28.4	13.8	1.1	51
C*	1.0	30	21.3	10.2	1.1	52
C*	1.0	30	14.2	13.8	0.03	3
C*	1.0	30	7.1	8.0	-	-
C	0.5	30	27.4	22.2	0.47	19
C	1.0	30	27.4	19.5	0.41	29
C	2.0	30	27.4	21.2	0.15	23
C	3.0	30	27.4	22.0	0.08	20
C	4.0	30	27.4	22.4	0.06	18
C	9.0	30	27.4	20.6	0.04	25
C	24.0	30	27.4	18.3	0.02	33

* *Leach liquor added to raffinate to vary initial amine concentration.*

TABLE 12

AMINE RELEASED FROM PRECIPITATED SOLIDS ARISING FROM NEUTRALISATION OF RAFFINATE B(AMINE CONCENTRATION 10.7 mg ℓ^{-1})

Contact Time (days)	Amine Concentration mg ℓ^{-1}	
	Solids + Neutralised Raffinate	Solids + Demineralised Water
0	<0.005	0
2	0.08	0.42
17	0.18	<0.05
35	<0.05	<0.05

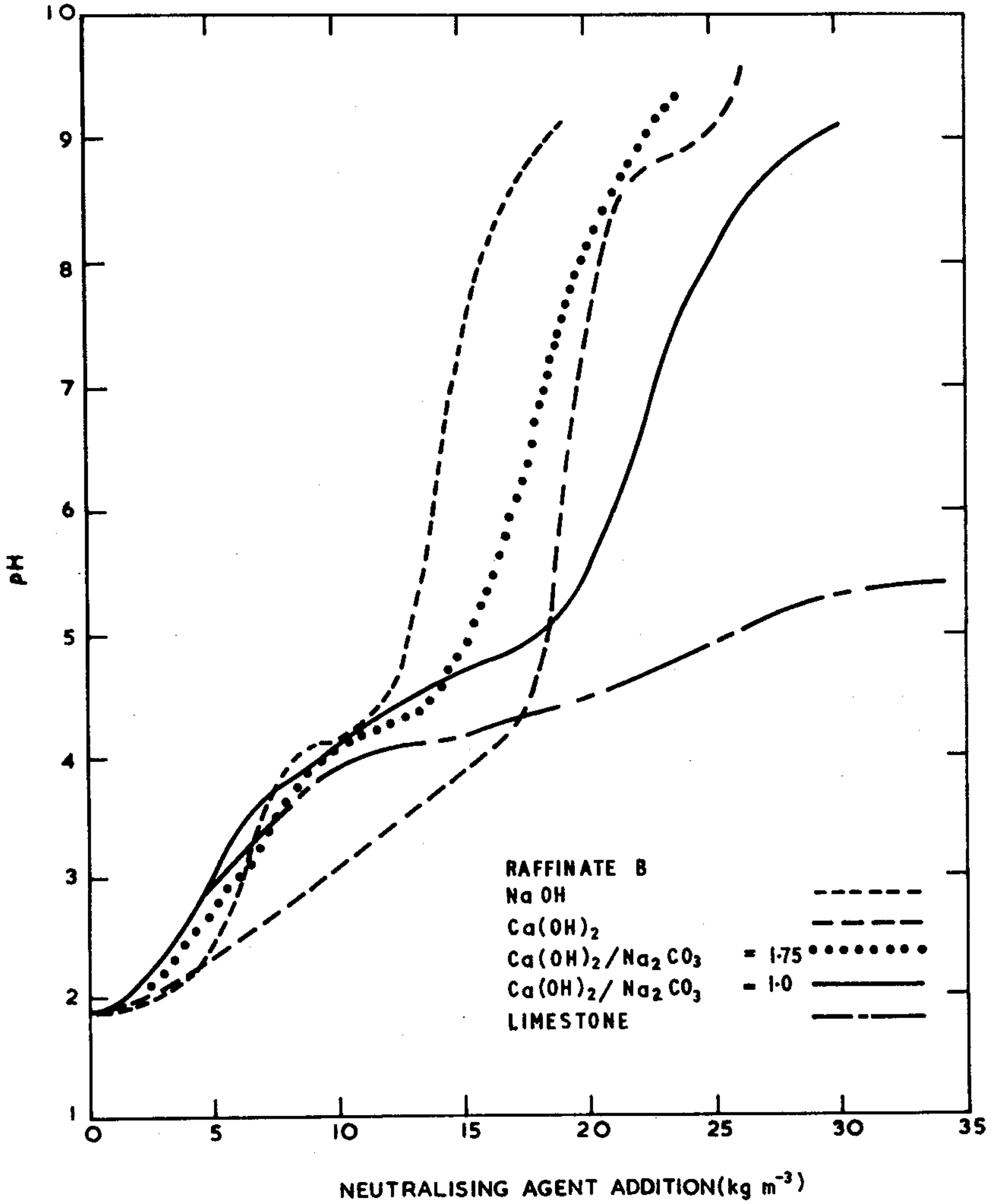

FIGURE 1. EFFECT OF REAGENT ADDITION ON pH DURING NEUTRALISATION

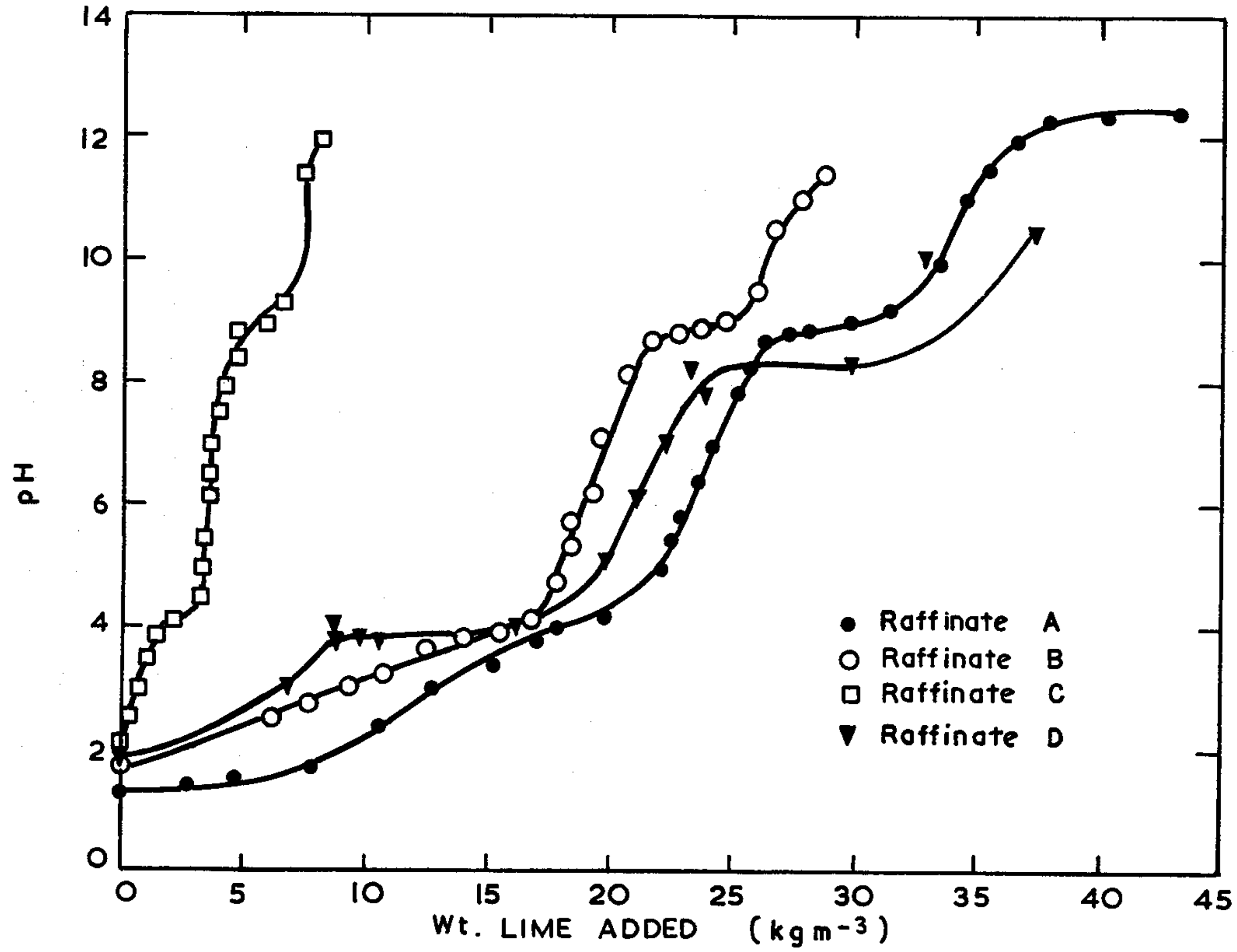

FIGURE 2. EFFECT OF RAFFINATE COMPOSITION ON NEUTRALISATION WITH LIME

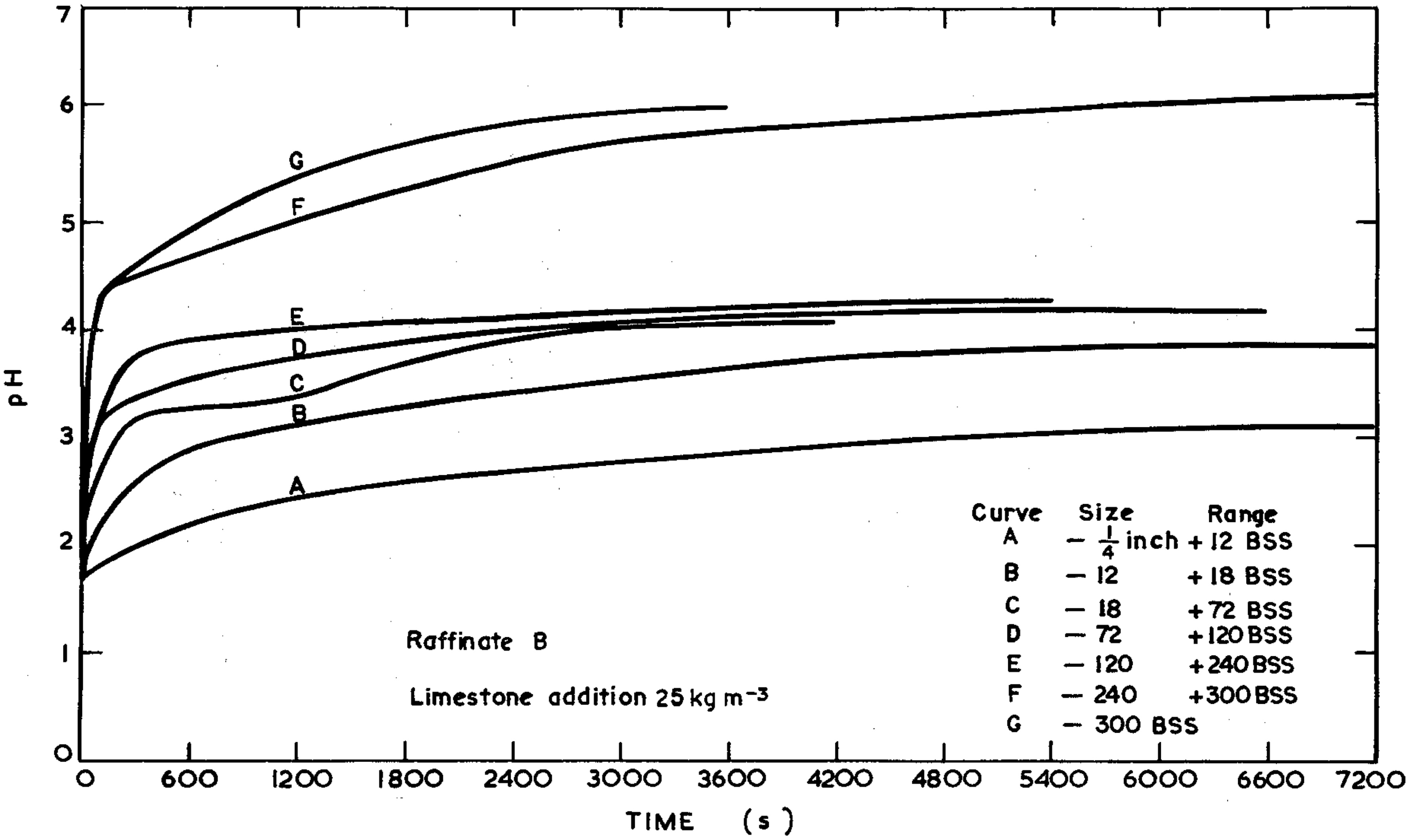

FIGURE 3. EFFECT OF PARTICLE SIZE ON NEUTRALISATION WITH LIMESTONE

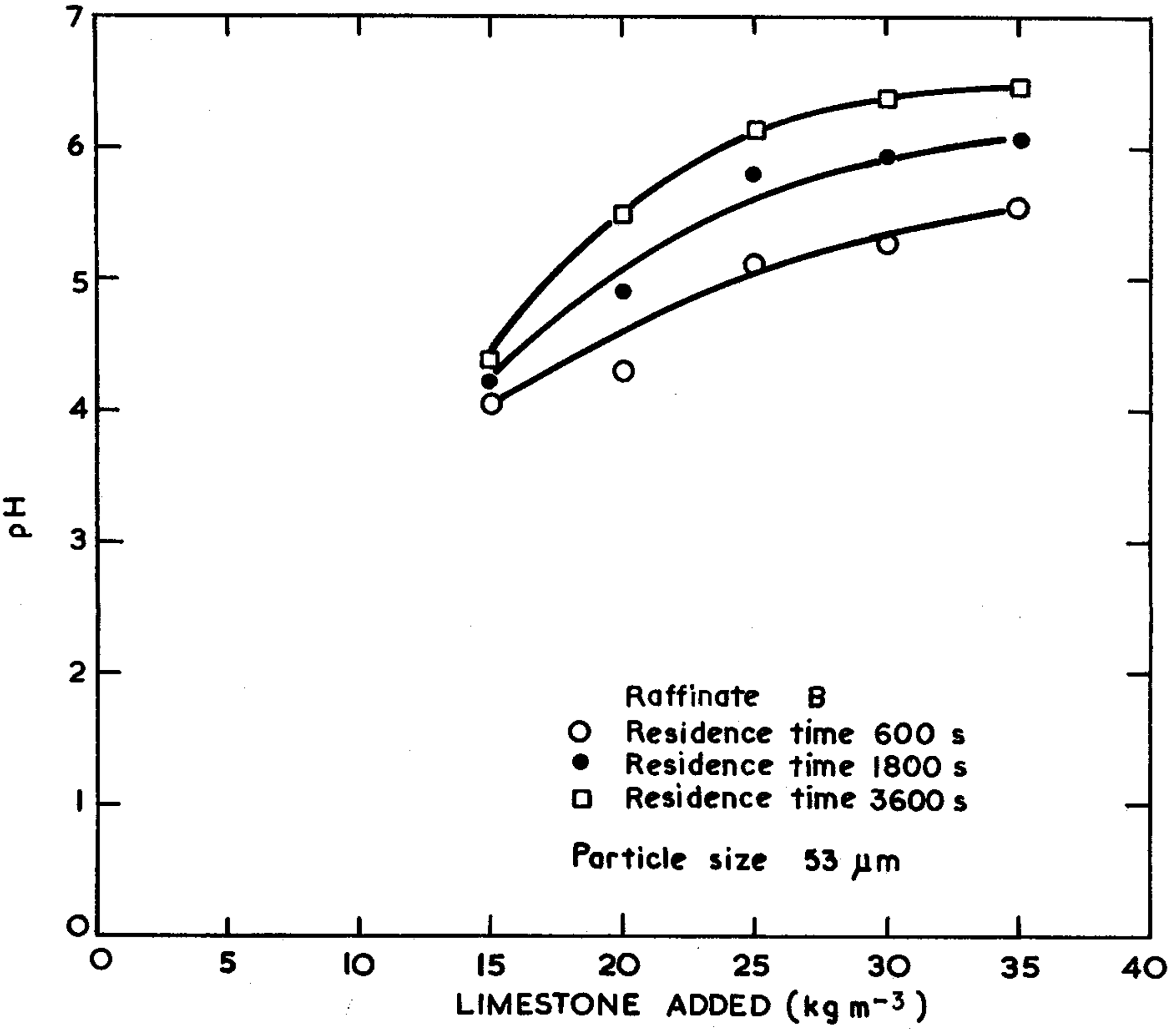

FIGURE 4. EFFECT OF RESIDENCE TIME ON NEUTRALISATION WITH LIMESTONE

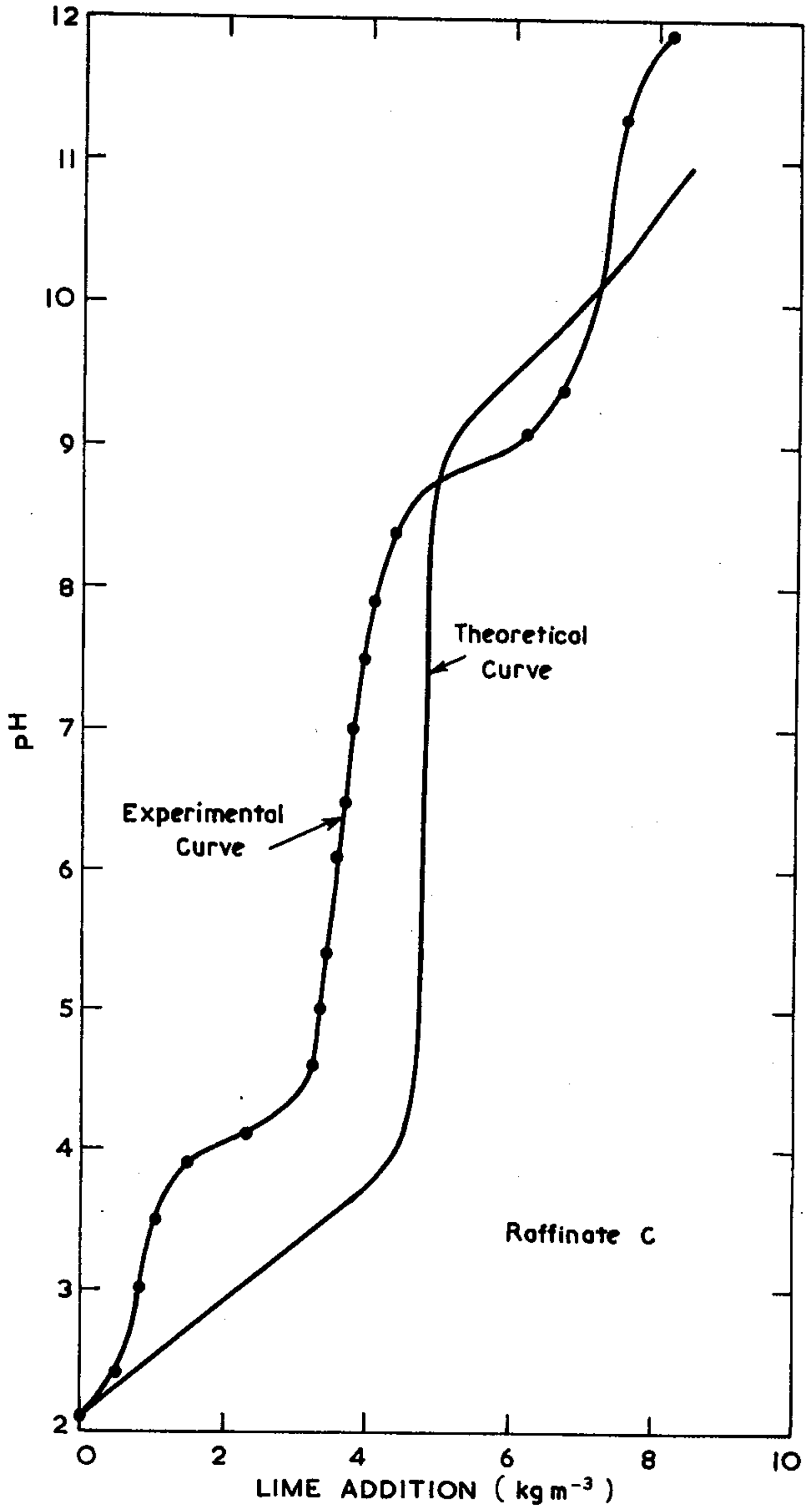

FIGURE 5. COMPARISON OF THEORETICAL AND EXPERIMENTAL NEUTRALISATION CURVES

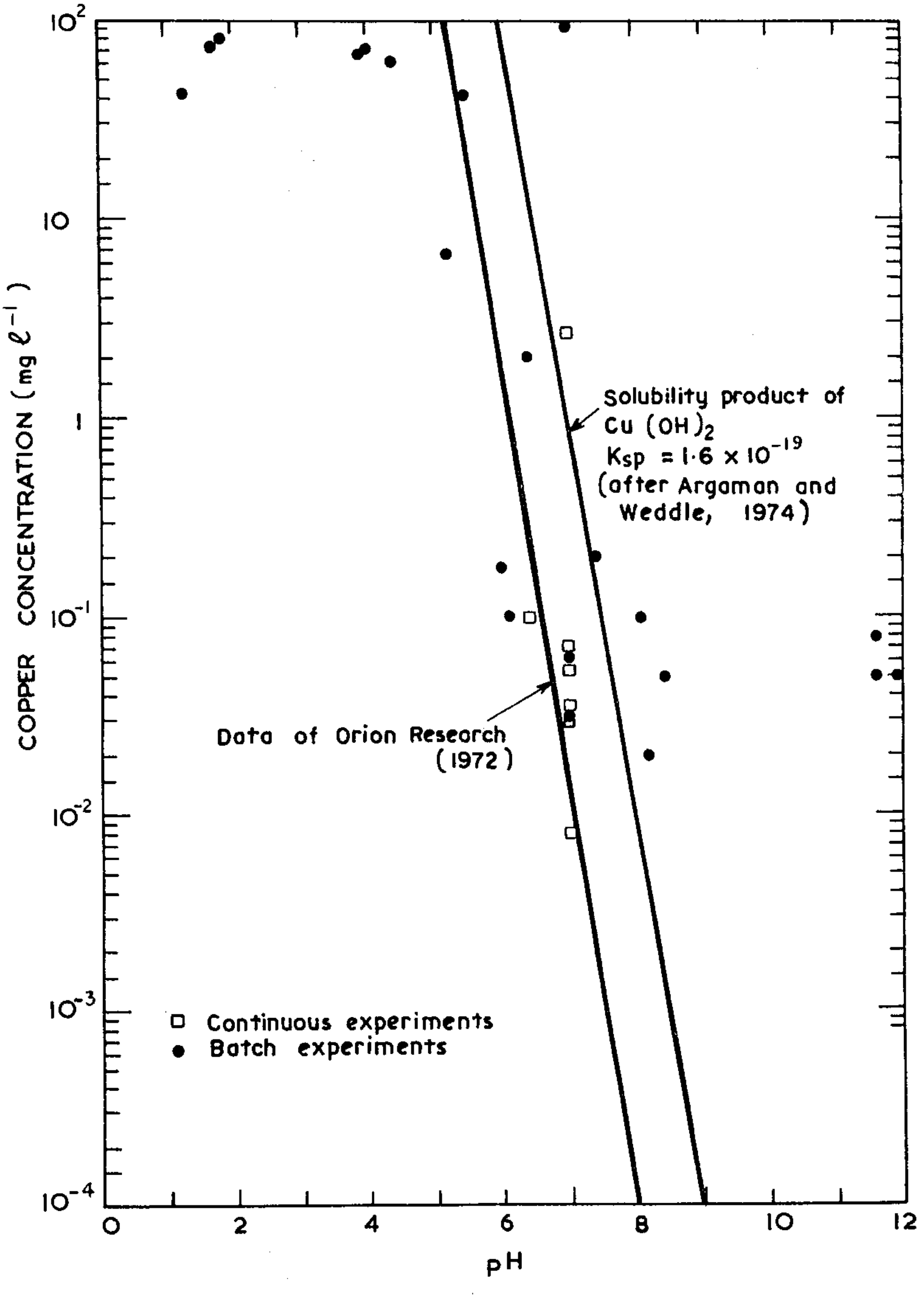

FIGURE 6. EFFECT OF pH ON COPPER PRECIPITATION

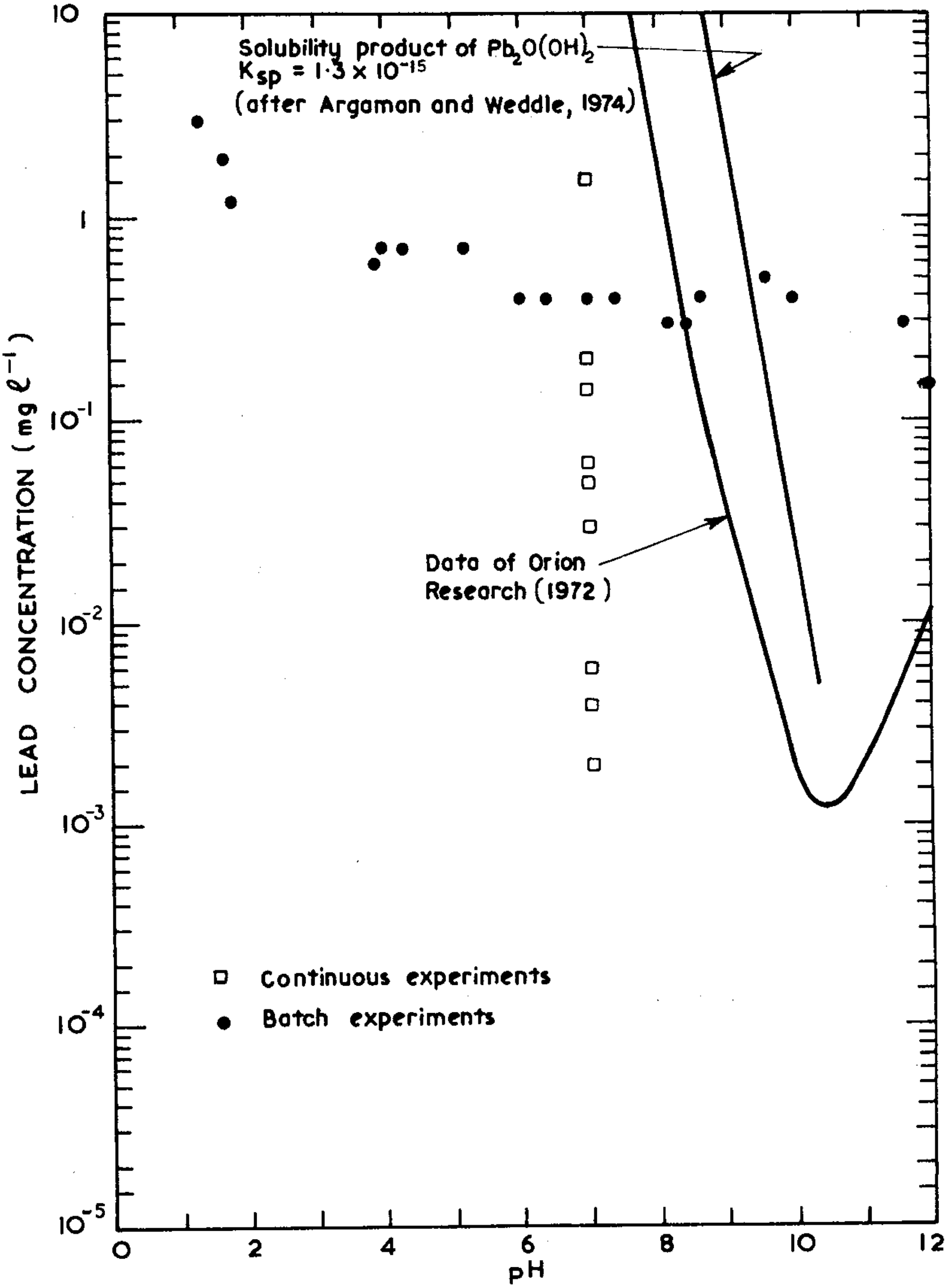

FIGURE 7. EFFECT OF pH ON LEAD PRECIPITATION

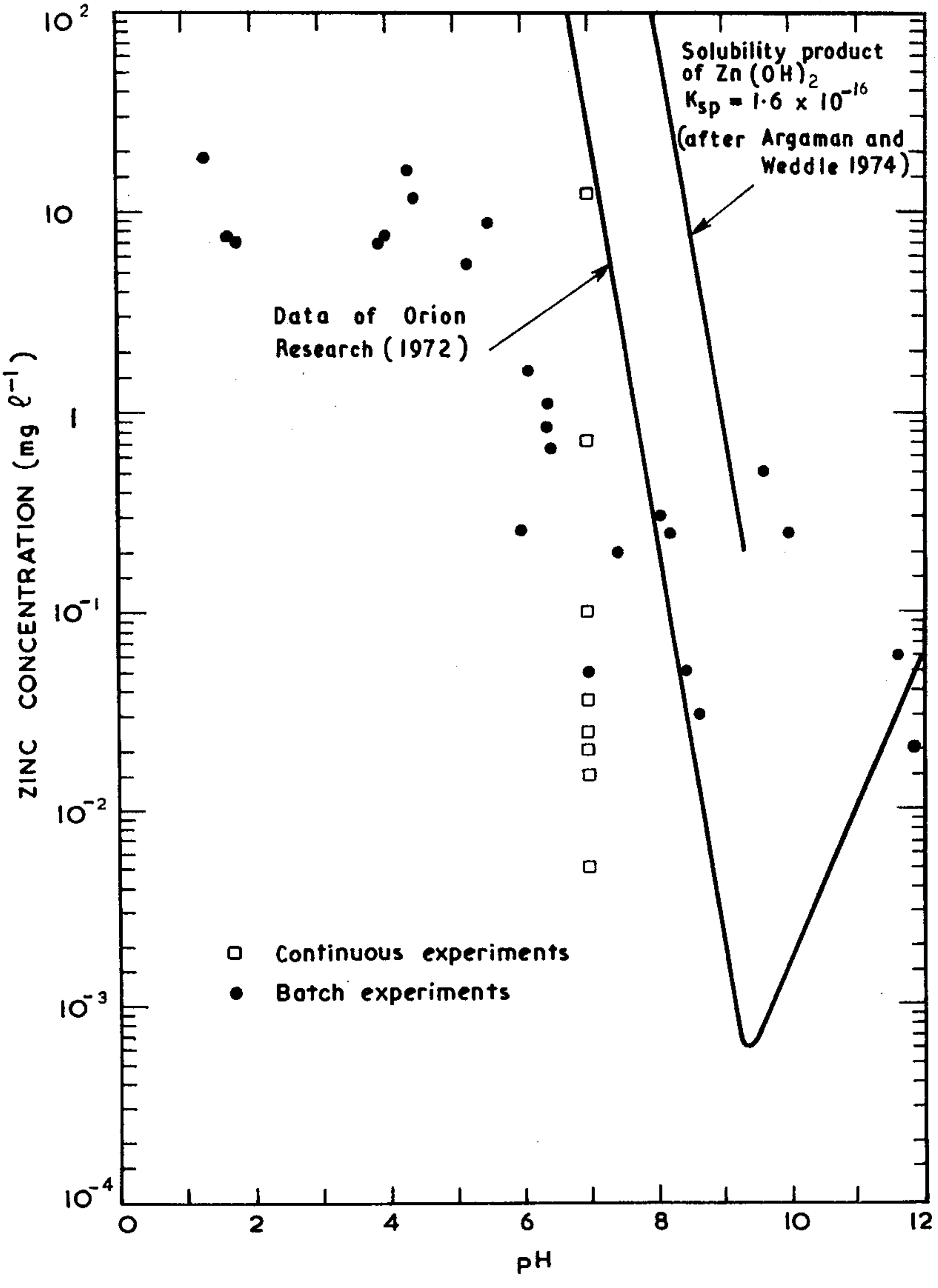

FIGURE 8. EFFECT OF pH ON ZINC PRECIPITATION

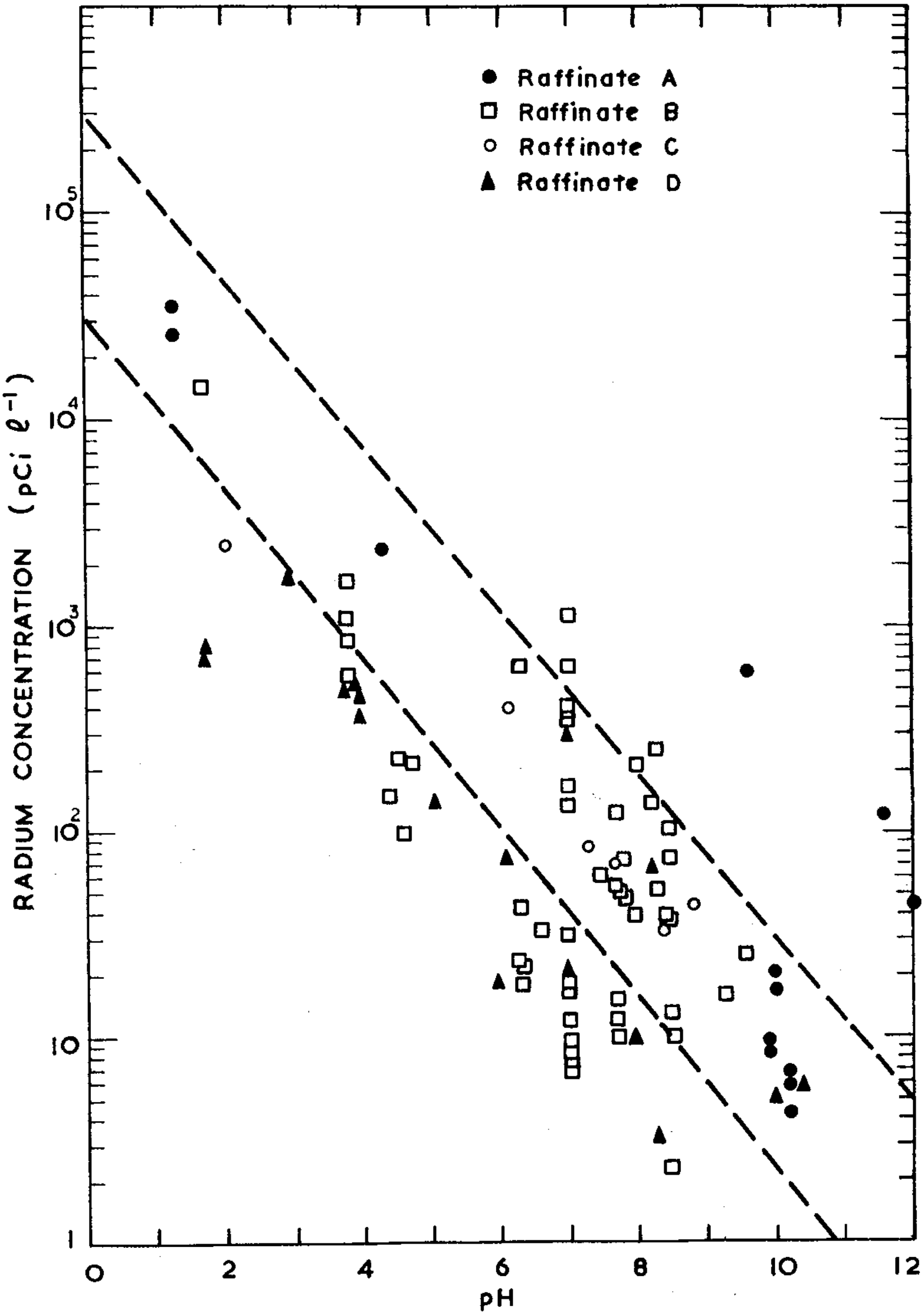

FIGURE 9. RADIUM CONCENTRATION AS A FUNCTION OF pH DURING NEUTRALISATION WITH LIME

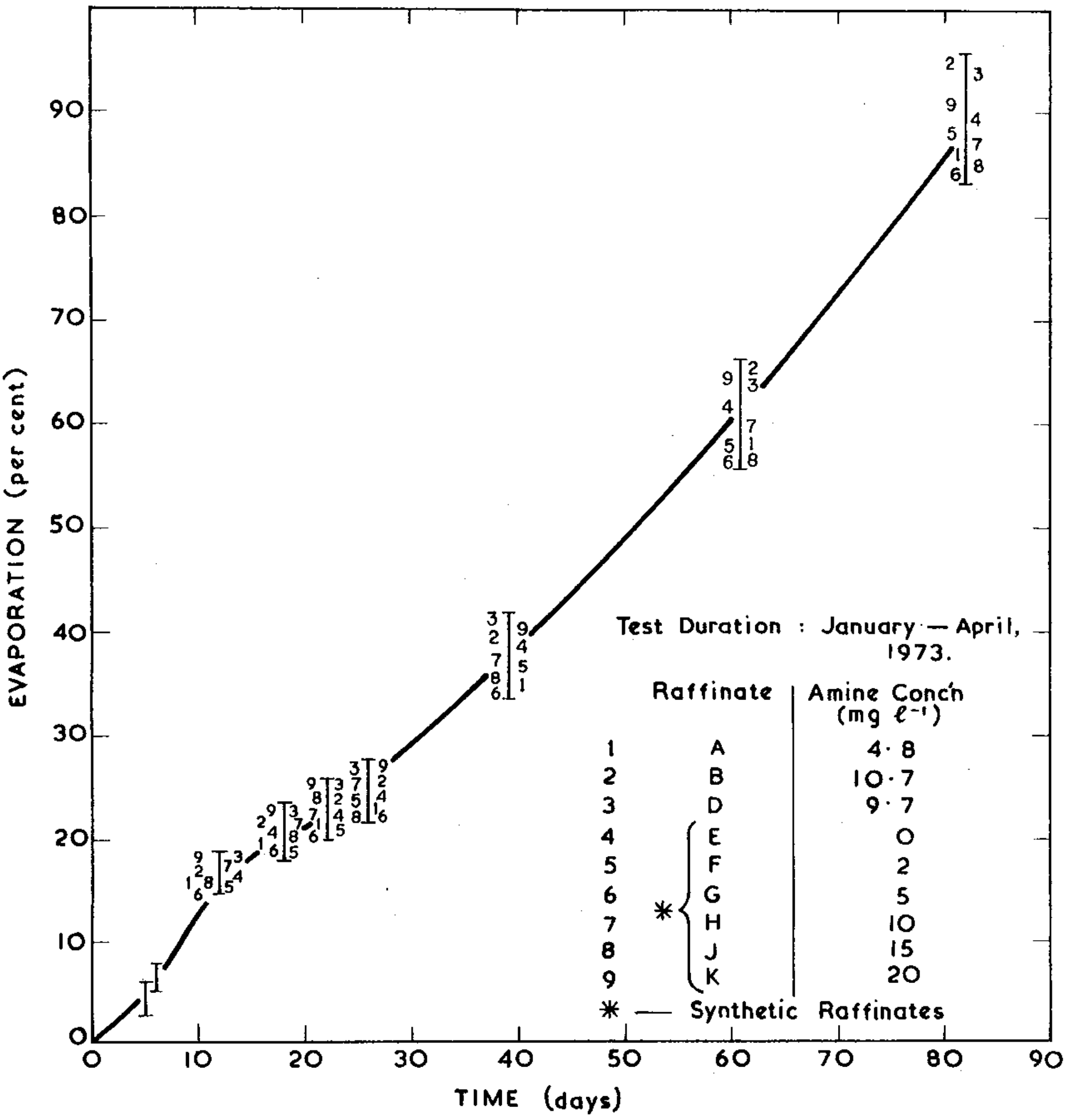

FIGURE 10. EVAPORATION OF RAFFINATE CONTAINING AMINE SOLVENT

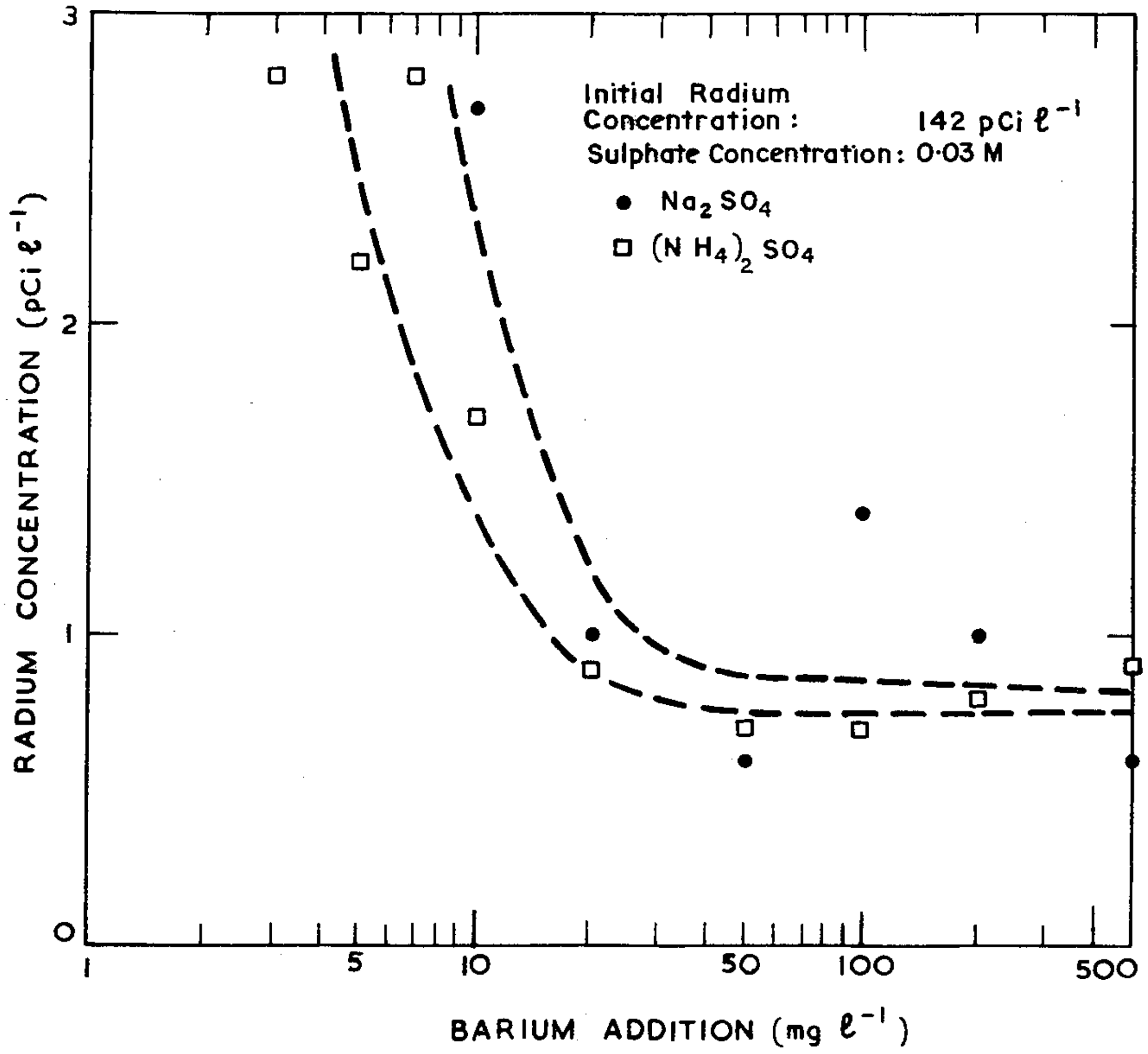

FIGURE 11. EFFECT OF BARIUM CONCENTRATION ON PRECIPITATION OF RADIUM FROM PIT WATER

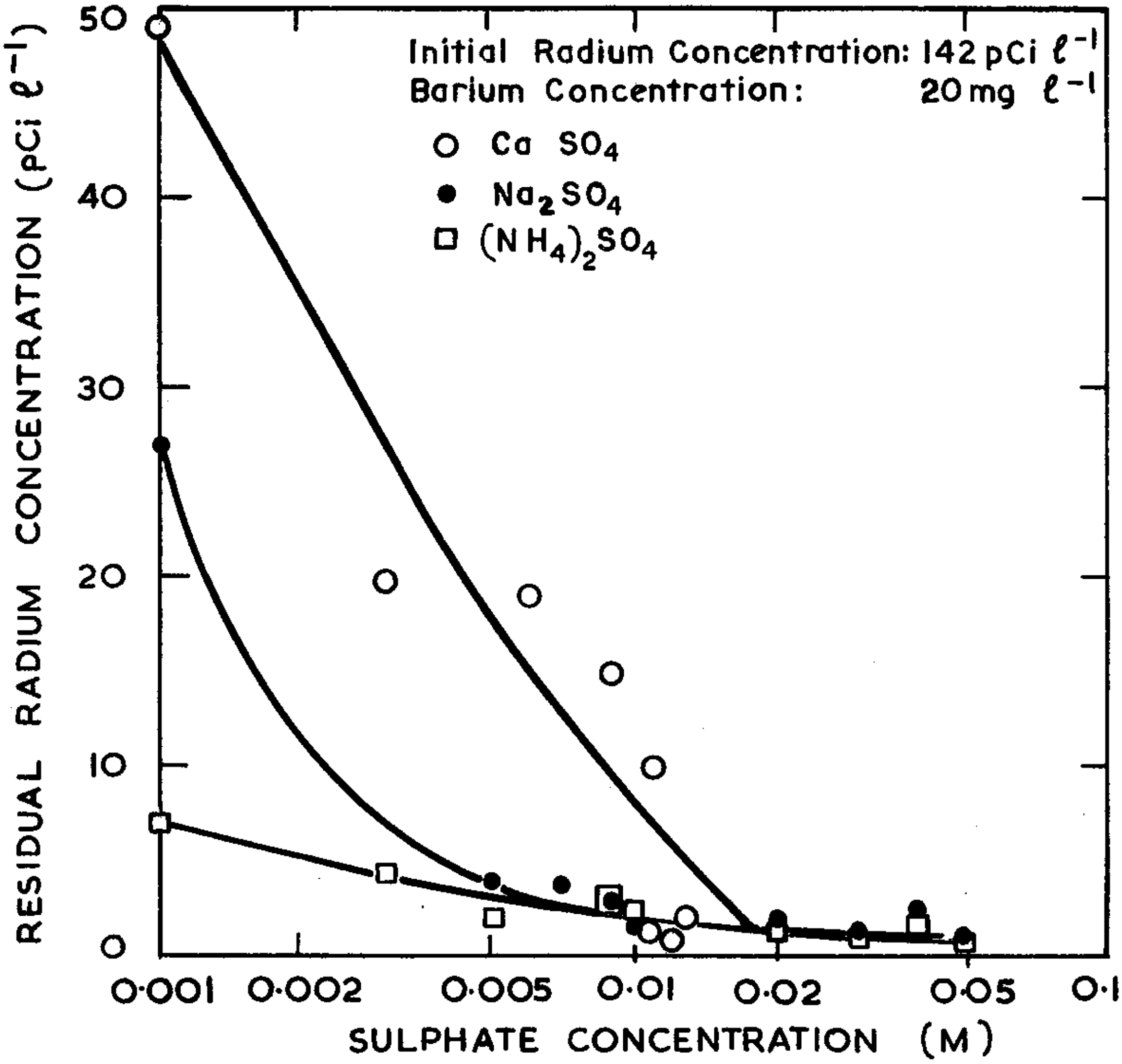

FIGURE 12. EFFECT OF SULPHATE CONCENTRATION ON PRECIPITATION OF RADIUM FROM PIT WATER