# THE REACTIVITY OF SOME ECONOMIC MINERALS WITH SOLID SODIUM HYDROXIDE

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by

Yeun Shik Kim, B.Sc.(Eng.), M.Sc.(Eng.)

Department of Mining and Mineral Technology,
Royal School of Mines,
Imperial College of Science and Technology,
London, S.W.7.

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## ABSTRACT

An improved method of processing minerals containing the more valuable metallic elements, such as monazite, wolframite, and columbite, with solid caustic alkali was examined. The process, described as 'fritting', is found to have technical and economic advantages over the conventional fusion and alkali leaching processes. In the process, the mineral concentrate, without further grinding, is intimately mixed with a slight excess of sodium hydroxide powder and heated to the minimum temperature necessary to achieve reaction. The products, in the form of loose aggregate, are leached with water to remove the soluble compounds.

The chemical and physical nature of the products was determined by chemical analysis, X-ray diffraction, electron-probe microscopy and infra-red spectroscopy. The products of reaction of the valuable minerals, after contact with water were:

(i) Monazite:- Sodium phosphate in solution; the rare earth oxides as a precipitate.

(ii) Wolframite:- Sodium tungstate and some manganese as sodium manganate in solution; the other part of manganese and the iron as oxide precipitates.

(iii) Columbite:- Sodium manganate in solution; sodium niobate, tantalate and iron, manganese oxides as a precipitate.

The principal advantages were:

(a) Reduction in alkali consumption ($^2/_3$ of that required for alkali leaching and $^1/_3$ of that required for the conventional fusion process).

(b) Particles of the size normally obtained by physical methods of separation reacted at a satisfactory rate.

(c) The products of reaction were readily leached with water, and the precipitated oxides were in a finely divided state

(~2μm) and reactive to acids.

The tungsten and tin contents of a wolframite-cassiterite mixture were separated by utilising the different rates of reaction of the two minerals.

The high reactivity observed with several minerals below the melting point of sodium hydroxide was interpreted as crystallographic phase changes in sodium hydroxide initiating the reaction, followed by liquifaction of more sodium hydroxide by the heat of reaction, thus giving good contact between the reactants for continued reaction.

## CONTENTS

PART I

PART II

PART III

# LIST OF FIGURES AND TABLES

Page No:

## a. Figures

Page No:

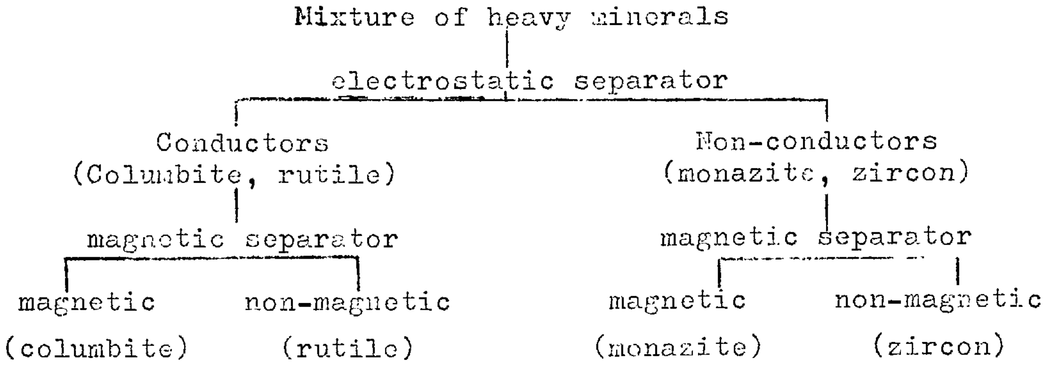
b. Tables

# INTRODUCTION

This thesis describes an improved method for chemically processing a number of valuable minerals with sodium hydroxide. The optimum processing conditions for reacting monazite, wolframite and columbite are described. These minerals contain high value metallic elements, such as the rare earths, thorium, tungsten, niobium and tantalum, which play an important role in modern industry in the production of special alloys, electronic equipment, nuclear materials, rockets and space craft.

## Winning Metals from Ores.

The minerals containing the rare earths, niobium, tungsten and the other relatively rare transition metals are widely distributed in the earth's crust. The first stage for winning one of these metals, once an ore has been discovered, is the mining of the ore body. The run-of-mine ore normally contains a small quantity of values with a large bulk of useless material and in this state it is unsuitable for economic processing by chemical methods. Thus, the second stage in winning the metals is physical separation of the valuable minerals from the useless minerals or 'gangue', a procedure known as mineral dressing. In mineral dressing the differences in the inherent physical properties of the minerals such as colour, specific gravity, surface chemical reactivity, magnetic and electrostatic properties are exploited; occasionally texture, hardness, radioactivity, etc. are also used. For example, the minerals of present interest occur in the rocks of igneous origin or their weathered materials which are often found in river or beach sand deposits. The mineral dressing method requires physical liberation of the mineral grains in a rock before separation and usually comminution of the ore is needed for this purpose. As the minerals in beach sands are almost completely liberated there is no need for the costly process of comminution and therefore this type of ore is preferred. The valuable minerals in the sands have a high specific gravity ( >5 ) hence they are readily separated from the large bulk of less-dense gangue minerals (S.G. <3) by simple gravity concentrators such as Humphrey spirals, tables or jigs. The concentration is normally achieved from sands containing up to approximately 3% of values and the enriched product contains 85 - 95% of vlues. The gravity method, however, is not adequate for the separation of individual 'heavy' minerals from each other because of the small difference in their specific gravities. Further concentration of individual minerals is achieved by magnetic and electrostatic separators in which differences in ferromagnetism and electrical conductance are exploited. For instance, a mixture of heavy minerals containing columbite, rutile, monazite and zircon can be (ideally) separated into individual minerals by the following scheme:



In practice, however, the differences in the properties are not so marked that a clear separation cannot be achieved, even with repeated 'cleaning' operations. In order to obtain sufficient grade (% of required component) of saleable products often a considerable portion of each mineral has to be discarded as unseparable; thus the process becomes uneconomical. There are a number of such cases where the physical methods fail. For instance, wolframite and cassiterite often occur associated together. Magnetic separation, the most practicable method for separating these minerals, is often spoilt by the presence of impurity iron in the grains of cassiterite. Other pairs of minerals, such as xenotime (or monazite) and zircon, or columbite and cassiterite are examples for which physical processing is not satisfactory. These pairs may be separated by the flotation method, in which surface chemical properties are utilized, however, the method has not been commercially established for these minerals. Chemical methods of separation are possible alternatives for these particular pairs of minerals. For this reason the possibility of selective chemical reaction of pairs of minerals was considered during this work and one example was investigated experimentally.

In the next major stage of winning valuable transition metals, the single mineral concentrates which have been prepared by mineral dressing are chemically processed to prepare suitable materials for the manufacturing industry.

The traditional pyrometallurgical methods of extracting metals such as iron, lead and zinc from their mineral concentrates are unsuitable for metals such as tungsten, niobium, rare earths, etc. because:-

(1) some of the metals, such as the rare earths, cannot be produced from their oxides by carbothermic reduction except at unreasonably high temperatures;

(2) others, such as tungsten, produce carbides in carbothermic reduction;

(3) the metals, e.g. tungsten and niobium, have such high melting points that they cannot be removed from a furnace as a fluid.

The methods which have to be adapted for the final stage of metal production are, for instance, hydrogen reduction of a high purity oxide to yield a high purity metal powder (e.g.

tungsten), fused salt electrolysis (e.g. rare earths), and reduction with sodium, magnesium, etc. (e.g. niobium, tantalum). However, some applications of these elements involve compounds such as the oxides.

No matter what the eventual application, a number of chemical stages are required to prepare and purify a suitable material, and they can be approximately divided into

(a) decomposition of the mineral,
(b) purification and preparation of a suitable pure compound of the required metal, and
(c) production of the metal or other final products from the pure intermediate compound.

The first step of chemical treatment of the minerals involves one of the following methods:
(i) leaching by acid or alkaline solution, sometimes under oxidizing or reducing condition, or by a dissolved reagent with which the metal forms a soluble complex;
(ii) roasting such as chlorination and sulphation, usually followed by leaching if the required product is not volatile;
(iii) dissolution in highly concentrated acids (such as $H_2SO_4$, HF, which ought not to be regarded as aqueous solutions) or in molten alkalis or salts (NaOH, $Na_2CO_3$, KOH, $KHSO_4$, etc.)
The choice of method depends on the physico-chemical nature of the concentrate, the final product required, and economic aspects of the operation. For example, columbite (iron manganese niobate and tantalate) is a refractory mineral which is not attacked by common acids except hydrofluoric acid. The mineral can be chlorinated whereby niobium chlorides are volatilized but this method is not widely adopted. Usually, the mineral is decomposed by concentrated hydrofluoric acid or molten alkali. (1) For monazite (cerium thorium phosphate) sulphuric acid leaching (2) and alkali leaching (3) methods are industrially practiced.

Wolframite (iron manganese tungstate) is also decomposed by aqueous alkaline solution under pressure at elevated temperatures for several hours from which relatively pure crystals of sodium tungstate are obtained. (4) Another tungsten mineral is scheelite (calcium tungstate) which is decomposed by acid leaching.(5)

After decomposition the next step involves purification and isolation of a suitable compound from the products of decomposition reaction. The ideal compound required is one which can be readily reduced to the metal (or reacted to form the required commodity), and which is easily separated from the solution, or a pure vapour phase condensate. Also, it is often stored or transported and, therefore, it should be stable, non-corrosive, non-volatile, etc.

General methods of purification are (i) fractional crystallization, (ii) selective precipitation, (iii) solvent extraction, (iv) ion exchange, and (v) distillation. For example the purification and separation of tantalum and niobium are often achieved by fractional crystallization of complex fluoride salts (marignac process)(6) which is based on the difference in the solubility of potassium fluotantalate ($K_2TaF_7$) and potassium fluoniobate ($K_2NbOF_5$ $H_2O$). The separation of individual elements from the rare-earth oxides is accomplished by either of the first four methods. (7)(8) Selective precipitation of hydrated thorium oxide from the rare-earths by partial neutralization is usually practiced when the oxides are dissolved in hydrochloric acid. Solvent extraction and ion exchange methods are used for the separation of the individual rare earths. The purification of tungsten is conducted mainly by repeated precipitation as calcium tungstate followed by dissolution in hydrochloric acid. Distillation is also used as the separation and purification means: niobium and tantalum chlorides are separated from the impure mixture of chlorides (9) containing iron and tungsten (boiling points:- $TaCl_5$:239°C, $NbCl_5$:249°C, $FeCl_3$:315°C, $WCl_6$:347°C).

Problems in the Decomposition-of-the-Mineral stage

In the current chemical methods of decomposition most minerals are processed either by acid or alkali. In the following Table 1 the typical features of the industrial processes for monazite, wolframite, etc. are compared:

Table 1. Comparison of the typical features of the current industrial processes for the minerals

| Features | Acid leaching | Alkali leaching | Alkali fusion |
|---|---|---|---|
| Particle size of mineral | as delivered or ground | finely ground (-300 mesh) | as delivered |
| Selectivity of extraction | poor | good | moderate |
| Retention time | long | long | short |
| Temperature of reaction | moderate (boiling temp.) | moderate (boiling temp.) | high |
| Excess reagent | >50% | >50% | >100% |
| Reactor material | expensive | expensive | cheap |

As shown in Table 1 the principal advantage of the alkali process over the acid process is selective dissolution of the components of the mineral; for example, the valuable component tungsten in wolframite $[(Fe,Mn)WO_4]$ is converted to soluble sodium tungstate whereas iron and manganese are precipitated as hydrated oxides (c.f. acid dissolves all the components). But important disadvantages are the need for excess alkali (e.g. columbite: >150% excess), fine-grinding (e.g. monazite and wolframite have to be reduced to -300mesh) or long reaction periods (e.g. monazite: 3-4hrs., wolframite: 5hrs.). In alkali fusion processes the products are in a fused mass which dissolves only slowly in water, hence they have to be crushed before water leaching. The fusion sometimes produce refactory compounds (e.g. acid insoluble rare-earth oxides from monazite). (3)(10)

Owing to the slow leaching rate the production scale is eventually limited. In most cases it requires a large capital investment in grinding facilities, high temperature furnaces (e.g. 800°C for columbite) or leaching equipment. In addition the operational cost may be high due to large excess consumption of the reagent and fuel, long reaction time, high temperature requirements, prolonged period of agitation etc.

In the work described in the remainder of this thesis particular attention has been given to a process for decomposing a number of minerals that overcomes some of the problems associated with the two alkali methods hitherto used commercially. In the published literature mention is often made of excess alkali without clearly stating the stoichiometric requirement. Presumably attempts have been made during the last half-century to reduce the alkali consumption, but no thorough scientific investigation of this aspect has been published.

Recently, Choi et. al. (11)(12) have discovered in the caustic treatment of zircon that the coarse mineral can be satisfactorily decomposed with reduced consumption of alkali and, furthermore, the products of reaction are obtained in a form of granular materials which disintegrated readily in water.

Such a process would be beneficial if it could be applied to other minerals. But, as the nature of the process was not established the possibility of applying it to other minerals cannot be predicted.

The possibility of decomposing monazite by a similar process was investigated first. The optimum conditions for complete, rapid reaction were found; the nature of the products and the sodium hydroxide requirements were also investigated. As the temperatures required for reaction of both zircon and monazite were much lower than those for the conventional fusion porcesses, and also the products were in a state amenable for further processing, the feasibility of the process for other minerals was investigated. From the empirical results a working theory has been devised for predicting the performance of other minerals in this process.

In the first half of the thesis the findings on monazite are described. In the later part the possibilities of processing, by selective reaction, pairs of minerals are discussed.

# PART I

## PRELIMINARY STUDIES

### 1. Reaction of a Mineral with Sodium Hydroxide

In the study of reactivity the two important aspects to be considered are

i) thermodynamic feasibility of reactions between various minerals and sodium hydroxide and

ii) the kinetic aspects of the reaction.

In the following section the thermodynamic feasibility is considered first and the factors affecting the rate of reaction are discussed next.

### 1.1 Thermodynamic feasibility

In order to assess the thermodynamic feasibility of the reaction of various minerals with solid sodium hydroxide information on the Gibbs free energy change of the reaction is required. This information can be obtained from calculation. For this purpose data on the free energy of formation for the various compounds involved in the reaction are required. But, the required data for many of the compounds encountered in the present study have not been determined. Since the value of the heats of formation for some compounds are available an attempt has been made to calculate the heat of reaction first and then deduce the entropy change and hence the Gibbs free energy change. In the calculation of the heat of reaction an estimated value of heat of formation has been used for some compounds where the necessary information is lacking.

### Estimation of heat of formation

The heat of formation of a compound oxide from its elements is equal to the sum of the heats of formation of the component oxides plus the heat of formation of the compound from the component oxides. The heats of formation for the simple oxides are known. Hence, if we can estimate the heat of formation of a compound from the component oxides, the heats of formation of a compound from its element can be obtained with reasonable accuracy. The compounds of present interest are double oxides made up of two simple oxides (e.g. $Na_2O.CeO_2$, $FeO.Nb_2O_5$, etc.). The reaction of a strong base oxide and a strong acid oxide involves a large heat of reaction (e.g. $^3/2Na_2O + {}^1/2P_2O_5 = Na_3PO_4$ $\Delta H^o_{298} = -131$kcal). Whereas the heat involved in the reaction between oxides of weakly basic and weakly acidic character is small (e.g. $FeO + TiO_2 = FeTiO_3, \Delta H^o_{298} = -7$kcal). In the reaction between oxides of weak base and strong acid or oxides of strong acid and weak base the heat involved would be in between.

(e.g. $Na_2O + Fe_2O_3 = Na_2Fe_2O_4, \Delta H^o_{298} = -45$kcal).

Hence, in the estimation of the heats of formation of compounds for which the data are lacking these properties for the component oxides have been taken into consideration, and a value of the heat of combination of two similar oxides has been adopted. For example, the heat of formation of $Na_2CeO_3$ from its elements was calculated as follows:

$$2Na + {}^1/2\ O_2 = Na_2O \qquad \Delta H^o_{298} = -99\text{kcal}$$

$$Ce + O_2 = CeO_2 \qquad \Delta H^o_{298} = -260\text{ kcal}$$

$$Na_2O + CeO_2 = Na_2CeO_3 \qquad \Delta H^o_{298} = -54\text{ kcal}^{*}$$

$$2Na + Ce + {}^3/2\ O_2 = Na_2CeO_3 \qquad \Delta H^o_{298} = -413\text{ kcal}$$

* The value is estimated from the reaction:

$Na_2O + SiO_2 = Na_2SiO_3, \Delta H^o_{298} = -54$kcal.

Other compounds for which the heats of formation from their elements are lacking have been estimated in a similar way. The known standard heats of formation and the estimated values used for the calculation of the heats of reactions are shown in Table 2.

## Table 2. Heat of Formation

| Compounds | $\Delta H^{\circ}$ form. from elements kcal/mole | Notes. |
|---|---|---|
| $CePO_4$ | -419(est.) | a |
| $FeWO_4$ | -285(est.) | a |
| $MnWO_4$ | -314(est.) | a |
| $Fe(NbO_3)_2$ | -519(est.) | b |
| $Fe(TaO_3)_2$ | -553(est.) | b |
| $FeTiO_3$ | -295 | Ref.(13) |
| $FeCr_2O_4$ | -342 | Ref.(14) |
| NaOH | -102 | Ref.(14) |
| $Na_3PO_4$ | -413 | Ref.(14) |
| $H_2O(g)$ | - 58 | Ref.(14) |
| $Na_2WO_4$ | -395 | Ref.(14) |
| $Na_2MnO_4$ | -274 | Ref.(14) |
| $Na_3NbO_4$ | -461(est.) | d |
| $Na_3TaO_4$ | -478(est.) | d |
| $NaFeO_2$ | -170 | Ref.(15) |
| $Na_2CrO_4$ | -317 | Ref.(14) |
| $Na_2TiO_3$ | -372(est.) | c |

Note:

a. Estimated by adoption of the following values (14):
$^1/2Fe_2O_3 + ^1/2P_2O_5 = FePO_4 \quad \Delta H^{\circ}_{298} = -21$kcal.

b. Ditto: $FeO + Cr_2O_3 = FeCr_2O_3 \quad \Delta H^{\circ}_{298} = -1$ kcal.

c. Ditto: $Na_2O + SiO_2 = Na_2SiO_3 \quad \Delta H^{\circ}_{298} = -54$kcal.

d. Ditto: $^3/2Na_2O + ^1/2V_2O_5 = Na_3VO_4 \quad \Delta H^{\circ}_{298} = -85$kcal.

## Thermodynamic feasibility of reaction

The calculated heats of reactions for various minerals with sodium hydroxide are shown with the respective reactions in Table 3. All the minerals under investigation evolve heat in the reaction with solid sodium hydroxide.

From the calculated heat of reaction the change in Gibbs free energy of reaction, $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$, can be evaluated for the particular system under investigation. Since the reaction system involves mostly condensed phases the change in entropy would be mainly influenced by the gaseous phases involved i.e. oxygen in the reactant and water vapour in the product. As the value involved with the water phase is greater than that of oxygen in all the reactions the change in entropy would result a positive value ($\Delta S>0$). Hence, the value in $\Delta G^{\circ}$ would remain as negative with even greater negative value. For example, in the reaction of monazite,

$$2CePO_{4(c)}+10NaOH_{(c)}+\tfrac{1}{2}O_{2(g)}= 2Na_3PO_{4(c)}+2Na_2CeO_{3(c)}+5H_2O_{(g)}$$

$$\Delta G^{\circ}_{298}= -178-[298(5 \times 0.05 - 0.025)] \approx -246\text{kcal.}$$

In other reactions as well an increase in $-\Delta G^{\circ}$ is expected. In other words, all the reactions give negative values in $\Delta G^{\circ}$ (reaction) hence, the reactions are thermodynamically feasible under standard conditions.

For the reactions at above the room temperature, similar treatment can be made. The variation in $\Delta H^{\circ}$ (formation) against temperature is small and it can be neglected in the present systems. As the value of $T\Delta S^{\circ}$ would remain positive and moreover, increase, the thermodynamic conditions for the reactions are expected to be more favourable at higher temperatures than at $298^{\circ}K$.

## Table 3. Heats of Reaction of Various Minerals with Sodium Hydroxide at 298°K

Monazite:

$$2CePO_{4(c)}+10NaOH_{(c)}+{}^{1}/{}_{2}O_{2(g)} = 2Na_3PO_{4(c)}+2Na_2CeO_{3(c)}+5H_2O_{(g)}$$

$$\Delta H^{o}_{298} = -178 \text{ kcal.}$$

Wolframite:

$$FeWO_{4(c)}+3NaOH_{(c)}+{}^{1}/{}_{4}O_2 = Na_2WO_{4(c)}+NaFeO_{2(c)}+1.5H_2O_{(g)}$$

$$\Delta H^{o}_{298} = -34 \text{ kcal.}$$

$$MnWO_{4(c)}+4NaOH_{(c)}+{}^{1}/{}_{2}\ O_2 = Na_2WO_{4(c)}+Na_2MnO_{4(c)}+2H_2O_{(g)}$$

$$\Delta H^{o}_{298} = -63 \text{ kcal.}$$

Columbite:

$$Fe(NbO_3)_{2(c)}+ 7NaOH_{(c)}+{}^{1}/{}_{4}\ O_{2(g)} = 2Na_3NbO_{4(c)}+NaFeO_{2(c)}+3.5H_2O_{(g)}$$

$$\Delta H^{o}_{298} = -63 \text{ kcal.}$$

$$Fe(TaO_3)_{2(c)}+7NaOH_{(c)}+{}^{1}/{}_{4}\ O_{2(g)} = 2Na_3TaO_{4(c)}+NaFeO_{2(c)}+3.5H_2O_{(g)}$$

$$\Delta H^{o}_{298} = -62 \text{ kcal.}$$

Chromite:

$$FeCr_2O_{4(c)}+5NaOH_{(c)}+{}^{7}/{}_{4}\ O_{2(g)} = 2Na_2CrO_{4(c)}+NaFeO_{2(c)}+2.5H_2O_{(g)}$$

$$\Delta H^{o}_{298} = -97 \text{ kcal.}$$

Ilmenite:

$$FeTiO_{3(c)}+3NaOH_{(c)}+{}^{1}/{}_{4}\ O_2 = Na_2TiO_{3(c)}+ NaFeO_{2(c)}+1.5H_2O_{(g)}$$

$$\Delta H^{o}_{298} = -28 \text{ kcal.}$$

## 1.2 Factors affecting the rate of reaction

Of factors affecting the rate of a reaction the following factors may be specifically important for a reaction system where mineral and solid sodium hydroxide are encountered.

i) Degree of contact between the reactants:-
For a particular size of the particles of reactants and the ratio of reagent to mineral the contact points between the particles of reactants would be increased by intimate mixing and pressing, for example.

ii) Removal of product layer from the reaction surface:-
This may be mostly achieved by the mechanical action of water produced in the reaction as it escapes from the reaction surface under its own pressure.

iii) Transport of the reagent to the reaction site:-
This would be most facilitated by the local melting of sodium hydroxide due to the heat of reaction. All the reactions of the minerals with sodium hydroxide are exothermic. The heat evolvedin the reaction would tend to remain in the vicinity of the reaction site since the materials involved are poor conductors. Thus the adjacent, unreacted, sodium hydroxide could be heated and it might become a molten state. The heat produced by reaction of monazite, for example, with solid sodium hydroxide is about 18 kcal. per mole of sodium hydroxide consumed. This heat is much greater than the heat required to take the corresponding amount of the adjacent reactants, say, from 250°C to the melting point of sodium hydroxide and melt the sodium hydroxide: $\sim$5 kcal. Hence, at a certain temperature even below the melting point of sodium hydroxide (<320°C) local melting could be expected once the reaction had started. If molten sodium hydroxide is involved the reaction in a strict sense cannot be called solid - solid reaction but, since the phenomena would be limited to local sites and the whole system would remain unfused, it should

be separately treated from the total fusion reaction. The local melting of sodium hydroxide would facilitate the rate of reaction in three ways (a) the molten sodium hydroxide could penetrate the product layer more easily than the solid, (b) the contact with fresh surface of the mineral would be greatly improved, (c) the molten sodium hydroxide would probably be more reactive than the solid. This action of local melting would be enhanced as the temperature of the whole system approaches the melting point of sodium hydroxide.

iv) Temperature:- Apart from the effect on the state of NaOH temperature is expected to influence the rate of transport of (molten) sodium hydroxide and the chemical reaction of the mineral with the sodium hydroxide (Arrhenius law).

v) Particle size:- As the particle size of the mineral decreases the specific surface will increase and the distance between the mineral and the reagent will be shorter, hence the availability of the reagent at a particular extent of reaction would be greater giving rise to a faster rate of reaction.

## 2. A Preliminary Experimental Survey of the Reactivity of some Minerals by D.T.A.

In order to obtain quick information on the reactivity of a number of minerals with solid sodium hydroxide the technique of differential thermal analysis (D.T.A.) was employed. In D.T.A. the measured variable is the temperature difference between the sample and an inert (thermally stable) material, as they are heated. Thus, any thermal change which takes place fairly rapidly can be detected by a pair of thermocouples, one in the sample and one in the inert material. The effect is normally indicated by a peak in difference in temperature of the two thermocouples. Since all the economic minerals under investigation evolve heat when they react with sodium hydroxide (see Table 3), the temperature at which rapid reaction occurs can be detected in this way.

Various mixtures of minerals and sodium hydroxide were subjected to D.T.A. tests up to a temperature of 700°C. The information on the reactivity in terms of temperature, thus, has been obtained at the expense of relatively little time and effort. The material and procedure employed, and the test results are described in the following sections.

### 2.1 Mineral samples

The mineral samples used for the D.T.A. tests are described in Table 4. A few grams of each of the samples were prepared from the relatively high grade, coarse-grained crystalline material by further purification mostly by hand sorting, heavy liquid separation, magnetic and electrostatic separation. The identity of the material was confirmed by means of chemical analysis, optical and electron probe microscopy, and x-ray diffraction, whatever appropriate for the particular mineral. The details

Table 4. Mineral Samples used for D.T.A. tests.

| Minerals | source | purity | Method of identification |
|---|---|---|---|
| Apatite | Swedish | >95% | Chemical analysis |
| Cassiterite | Odegi, Nigeria | 90% | Chemical analysis and electron probe microscopy |
| Chromite | Zwartkop, S. Africa | 95% | " |
| Columbite | Nigerian | 95% | " |
| Garnet (Almandite variety) | unknown | 95% | Optical microscopy and electron probe microscopy |
| Hematite | Swedish | 95% | Chemical analysis and physical determination |
| Ilmenite | Unknown | 95% | Optical microscopy and electron probe microscopy |
| Magnetite | Unknown | 95% | Magnetic properties and chemical analysis. |
| Monazite | Korean | 95% | Chemical analysis, x-ray diffractometry and electron probe microscopy |
| Quartz | Unknown | 98% | Optical microscopy |
| Rutile | Australian | 95% | Optical and electron probe microscopy |
| Scheelite | Unknown | 95% | U.V.fluorescence and chemical analysis |
| Tourmaline | Unknown | >90% | Optical microscopy |
| Wolframite | Unknown | >90% | X-ray diffraction, chemical analysis |
| Xenotime | Nigerian | >90% | Chemical analysis and optical microscopy |
| Zircon | Unknown | >95% | Optical and electron probe microscopy |

on the individual minerals can be found in the table.

## 2.2 Methods

### Apparatus

The D.T.A. apparatus used for the present investigation was that built originally by Mr L. R. Barrett, Department of Chemical Engineering, Imperial College. The set-up consisted of 5 main parts: a tube furnace, a sample holder of two compartments fitted with two sets of thermocouple wires, a heating block, a D.C. amplifier and a chart recorder.

The original sample holder, which was made of sintered alumina containing minute pores, was not suitable for the present work because of the corrosive nature of molten sodium hydroxide. Therefore, it was replaced by a silver cell fabricated from a block of silver (12mm. x 24mm. x 14mm.) which had two holes drilled in it to contain sample and reference material. Another two small holes were made on each side of the compartments to install thermocouple wires (chromel-alumel) insulated by ceramic tubes. The design and the thermocouple arrangement are shown in Figs. 1 and 2, and Fig. 3 shows the sample holder arranged in the stainless steel heating block.

### Procedures

There are a number of experimental factors affecting the result of D.T.A. tests. The suggestions by Arens(16) have been taken into consideration in the preliminary runs and the following conditions were employed throughout the tests.

(i) Heating rate: 10 ± 1°C/min. as Mackenzie(17) recommended for the purpose of standardization.

(ii) Inert reference material: calcined alumina powder was used.

(iii)Temperature of the sample, not the reference material, was measured by means of a chromel-alumel thermocouple inserted

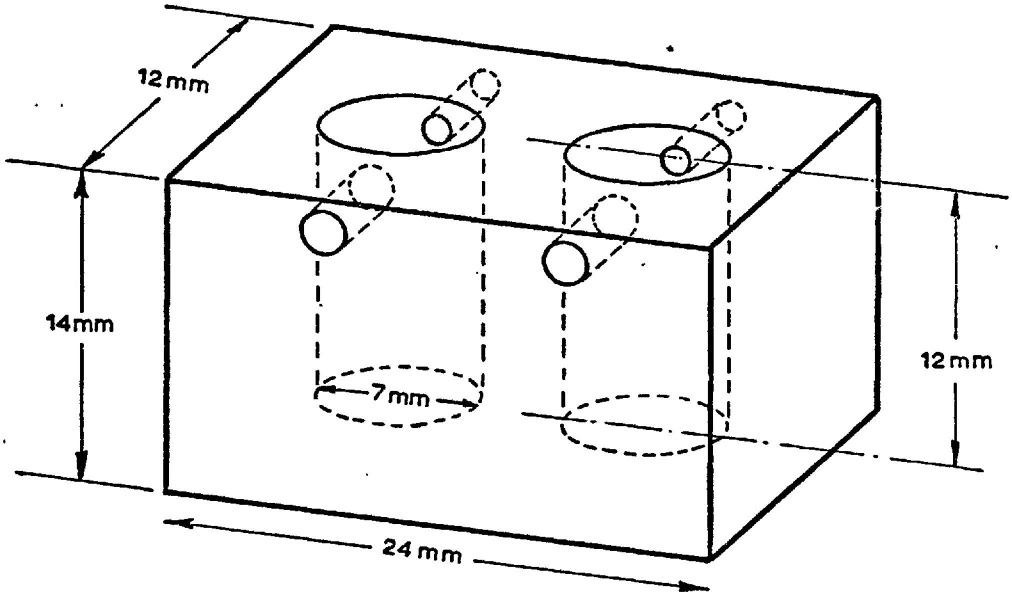


Fig.1 Sample holder for D.T.A.

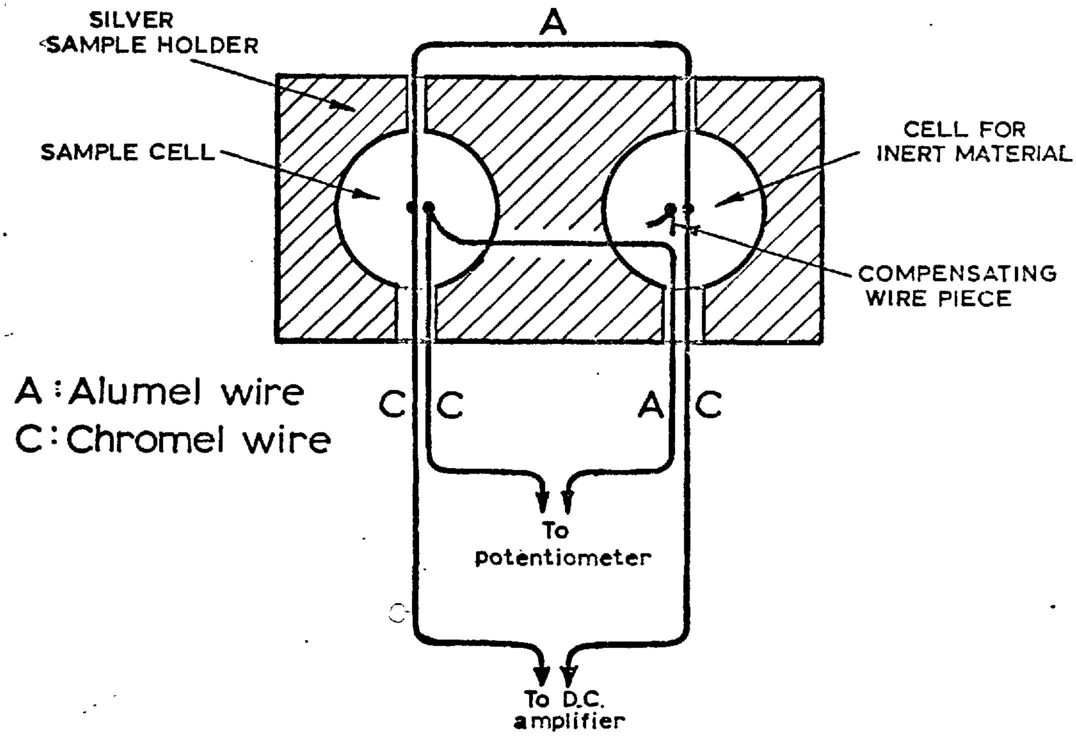


Fig. 2 Arrangement of thermocouple wires for D.T.A.

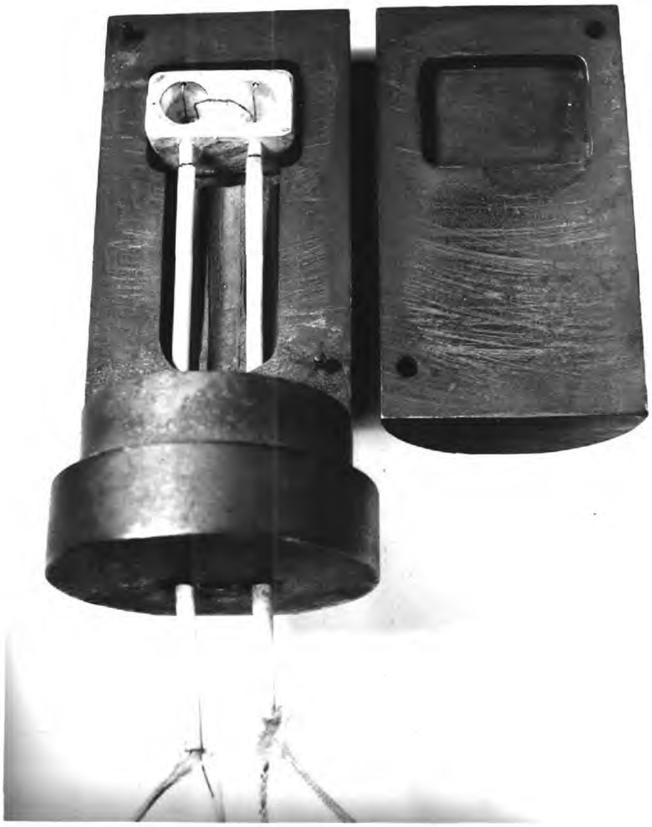


Fig. 3 Silver sample holder with thermocouples arranged in the stainless steel heating block. $^3/_4$ of actual size.

in the centre of the sample mixture.

(iv) Speed of chart recorder: 1 inch/10min.

(v) The test was conducted under atmospheric conditions.

The general procedure for the test was as follows: A pre-weighed quantity of sodium hydroxide in a glass tube (10mm. x 50mm.) with two small glass balls was mixed together with a separately weighed quantity of mineral sample by means of shaking. In this way a uniform mixture was obtained and the pick-up of moisture was minimised. The weight of sample used was in the range 0.4 - 0.6g. depending on the size and bulk density of the mixture. After placing the sample and the reference material in the cell, heating was started immediately and the temperature of the sample was measured by means of a potentiometer at two minute intervals. Some additional readings were also taken at any points where thermal changes were noted.

## 2.3 Results of D.T.A. tests on various mineral - NaOH mixtures

Eleven economic minerals (monazite, xenotime, apatite, wolframite, scheelite, rutile, ilmenite, columbite, zircon, chromite and cassiterite) and four associated gangue minerals (quartz, tourmaline, garnet and hematite) were examined. Two size ranges of the mineral, 72/300 mesh and -300 mesh B.S. were tested separately. An excess quantity of sodium hydroxide, approximately 50 to 100% over the stoichiometric requirement, was employed to ensure its reaction as well as to overcome some operational difficulties such as insufficient contact of thermocouple hot junction with the sample as the heating proceeded, especially on melting of the sodium hydroxide.

The D.T.A. thermograms showed that many minerals reacted at lower temperatures than the melting point of sodium hydroxide. The results are described under the three headings:

(i) those minerals which appear to react at much lower temperatures than the melting point of sodium hydroxide,

(ii) those which react approximately at the melting of sodium hydroxide and

(iii) those which require much higher temperatures in molten sodium hydroxide for reaction.

(i) Minerals with a low temperature peak

Those minerals which reacted in the temperature range below the melting point of sodium hydroxide were monazite $[(Ce,Th)PO_4]$, columbite $(Fe,Mn)[(Nb,Ta)O_3]_2$, wolframite $[(Fe,Mn)WO_4]$, hematite $(Fe_2O_3)$, garnet (Fe,Al,silicate), xenotime $(YPO_4)$, quartz $(SiO_2)$, tourmaline (a complex boron silicate) and apatite $[Ca_5(PO_4)_3F]$. The thermograms for these minerals are shown in Fig.4. The top curve in Fig. 4 shows the thermal change of sodium hydroxide itself. Hence, the first endothermic peak, at around 64°C which appears in all the thermograms, corresponds to the characteristic peak of sodium hydroxide caused by melting of sodium hydroxide monohydrate.

The peaks at around 290°C and 310°C are also characteristic peaks of sodium hydroxide which correspond respectively to the solid phase change $\alpha$-NaOH $\rightarrow \beta$-NaOH ( 280°C) and melting of $\beta$-NaOH ( 315°C).

It is interesting to observe that many of the minerals show their reactivities at low temperatures. Both the fine and coarse monazite indicated some reactivity at temperatures as low as 165°C (fine particles) and 185°C (coarse particles). The coarse monazite showed one more exothermic peak at 340°C. The endothermic peak at around 450°C. is probably due to some phase change associated with product phases as no change in weight was observed at the temperature (according to thermogravimetric analysis).

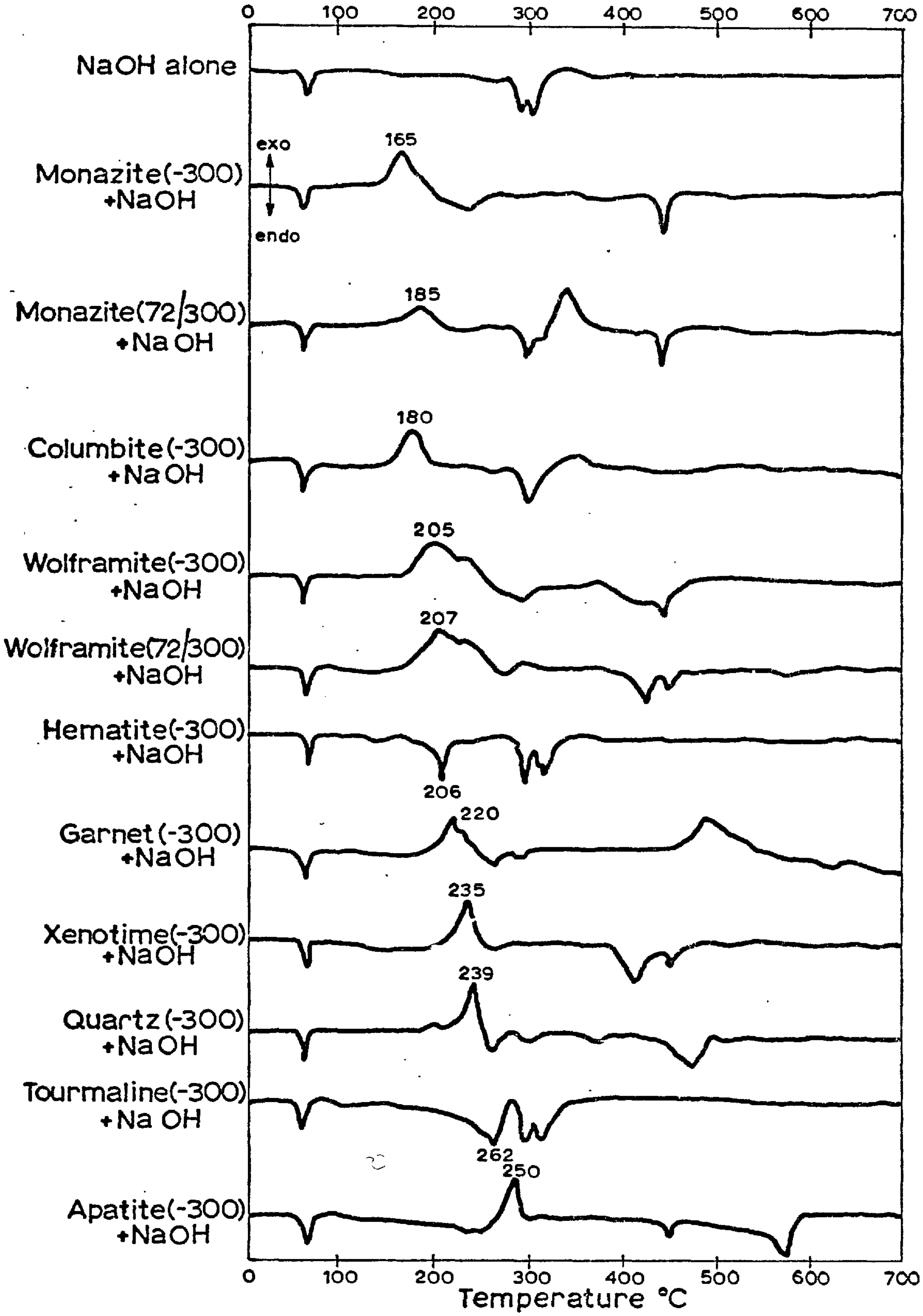


Fig. 4 D.T.A. curves for NaOH and various mineral-NaOH mixtures:- those minerals which show a reaction peak below the melting point of sodium hydroxide.

The temperatures at which the rest of minerals reacted were

| | |
|---|---|
| 180°C ... ... ... | columbite (fine particles) |
| 205°C, 207°C ... ... ... | respectively for the fine and coarse wolframite |
| 206°C ... ... ... | hematite (fine particles) |
| 220°C ... ... ... | garnet (fine particles) |
| 235°C ... ... ... | xenotime (fine particles) |
| 239°C ... ... ... | quartz (fine particles) |
| 262°C ... ... ... | tourmaline (fine particles) |
| 280°C ... ... ... | apatite (fine particles) |

The high temperature endothermic peaks, around 450°C, with wolframite and xenotime were found to be due to the fusion of the product phases.

### (ii) Minerals reacting on fusion of the sodium hydroxide

All the coarse particles of quartz, tourmaline, apatite, monazite, scheelite and xenotime reacted on fusion of the sodium hydroxide. The reactions were all exothermic except that of tourmaline. The peak temperatures ranged between 313°C and 345°C(see Fig.5).

### (iii) Minerals requiring a high temperature

The minerals which reacted between 400°C and 600°C were rutile (fine size at 425°C, coarse size at 571°C), garnet (at 490°C), coarse columbite (at 555°C), zircon (at 556°C) and chromite (both sizes at 565°C). The only reaction peak observed with the fine garnet was an endotherm. The zig-zag recording in the high temperature range was due to the slow evolution of a gaseous product (water) which indicated actual reaction but at a slow rate. Fig. 6 shows the thermograms for these minerals.

Ilmenite and cassiterite did not show any reaction peak irrespective of their size within the temperature tested (700°C),

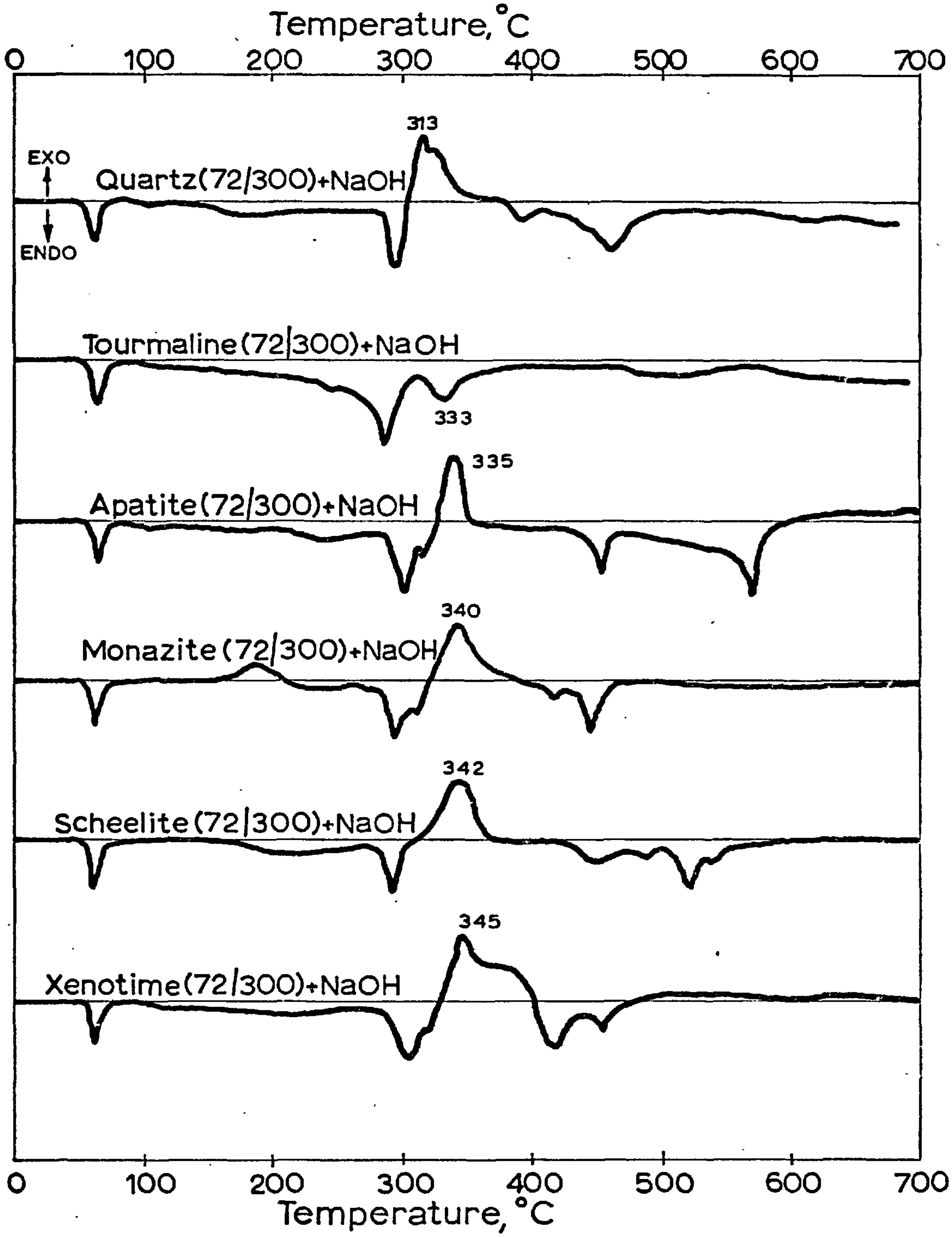


Fig. 5 D.T.A. Curves for various mineral-NaOH mixtures :- those minerals which show a reaction peak on melting of sodium hydroxide.

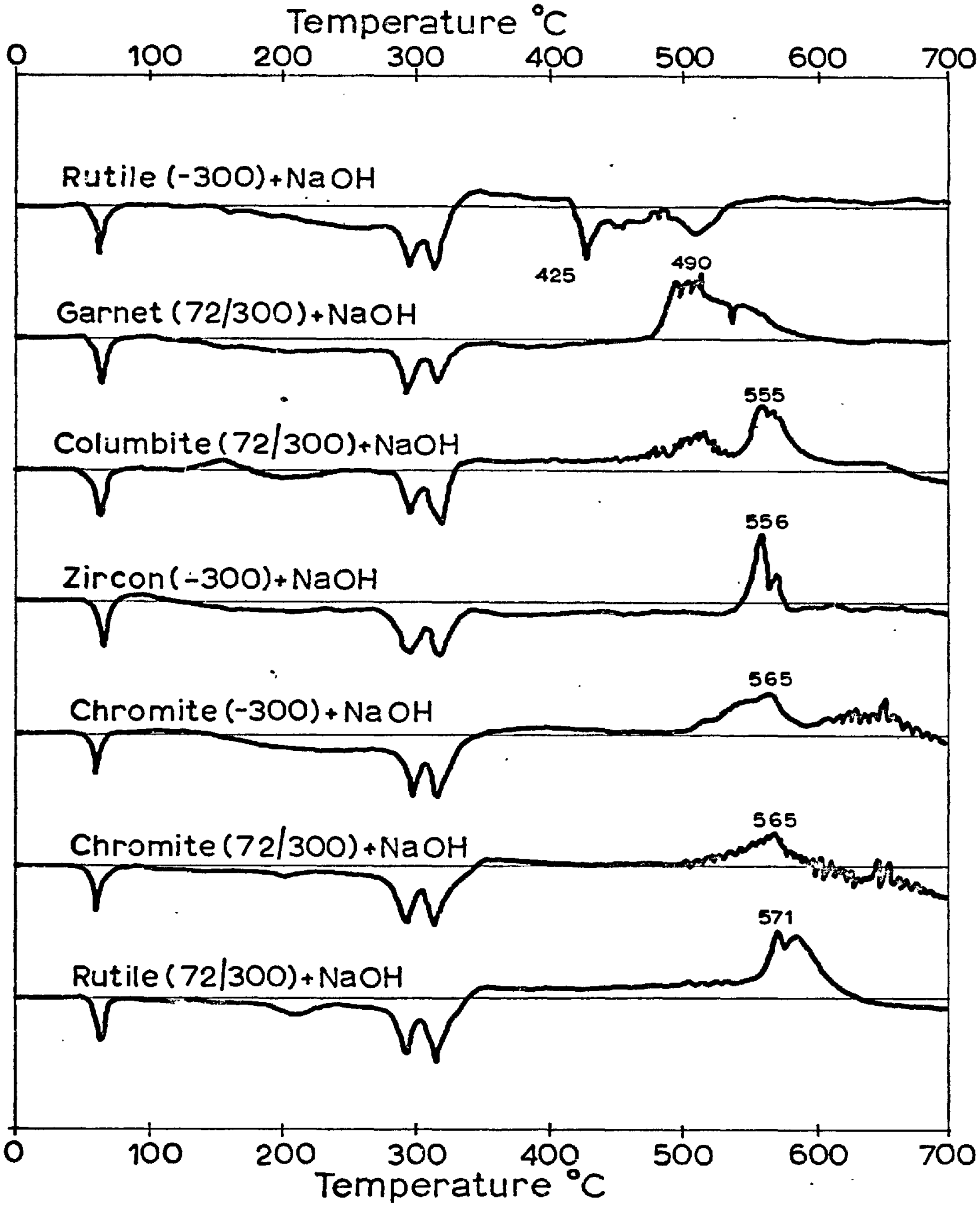


Fig. 6 D.T.A. Curves for various mineral-NaOH mixtures :- those minerals which show a reaction peak at moderately high temperatures of molten sodium hydroxide.

though some slow reaction with ilmenite was noted above 550°C by 'noise' recording. The fine hematite showed a reaction peak at a temperature low as 206°C (see Fig.4) but the coarse hematite did not show any reaction peak below 700°C. Thermograms for these minerals are shown in Fig.7.

A graphical summary of the reactivity of the minerals according to D.T.A. peaks, is given in Fig 8. The vertical column represents the temperature. The fine size of mineral (-300mesh) is shown on the left hand side and the coarse size (72/300) on the right hand side of the column. It is interesting to note that many minerals of fine particle size are densely populated in a temperature range from 160°C to 290°C indicating, apparently a solid-solid reaction. All the phosphates, tungstates, and silicates of coarse size react at around 300°C.

These data were used to select appropriate temperatures at which to study the various reactions in more detail.

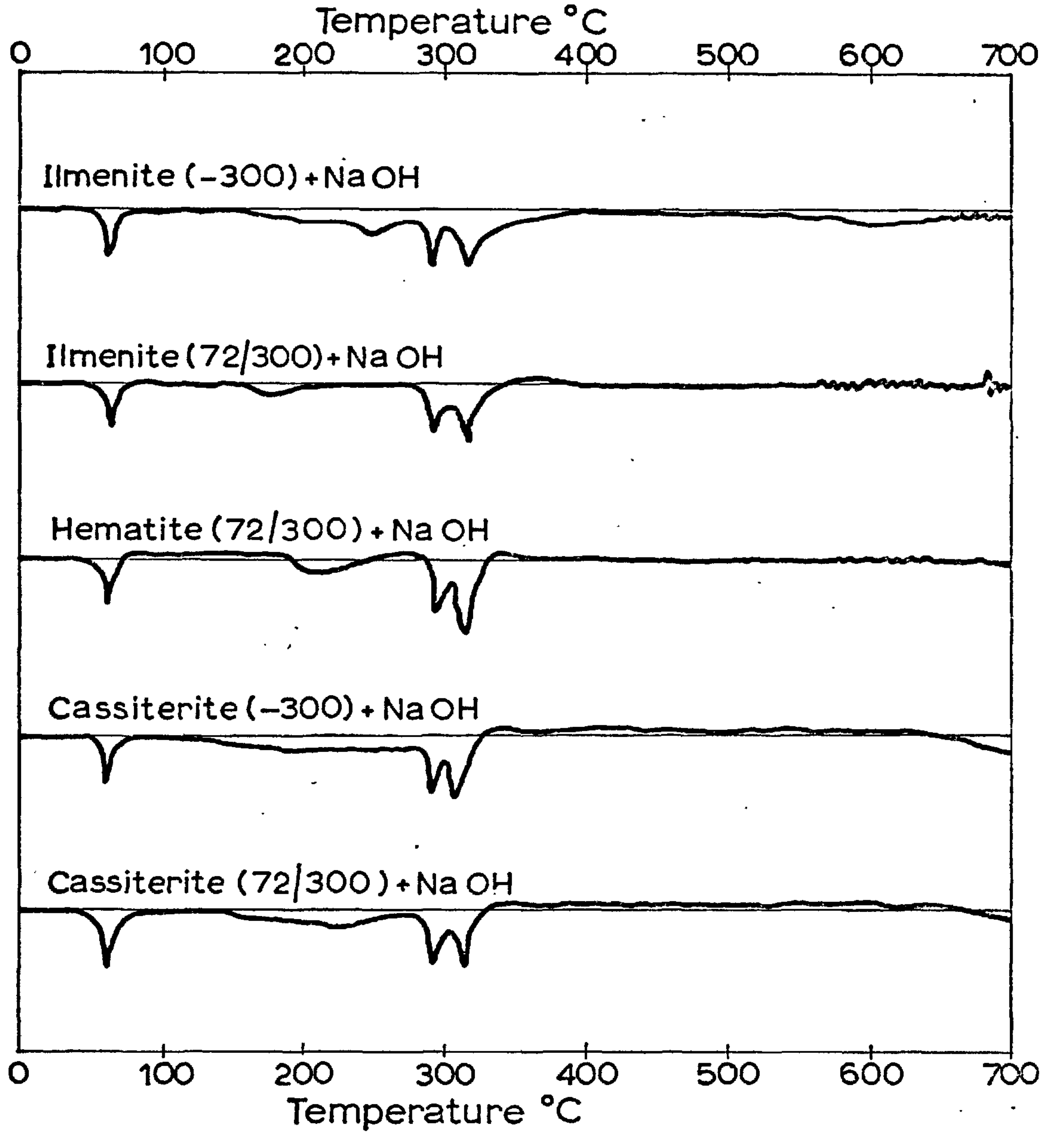


Fig. 7 D.T.A. curves for various mineral-NaOH mixtures :- those which do not show reaction peak below 700°C.

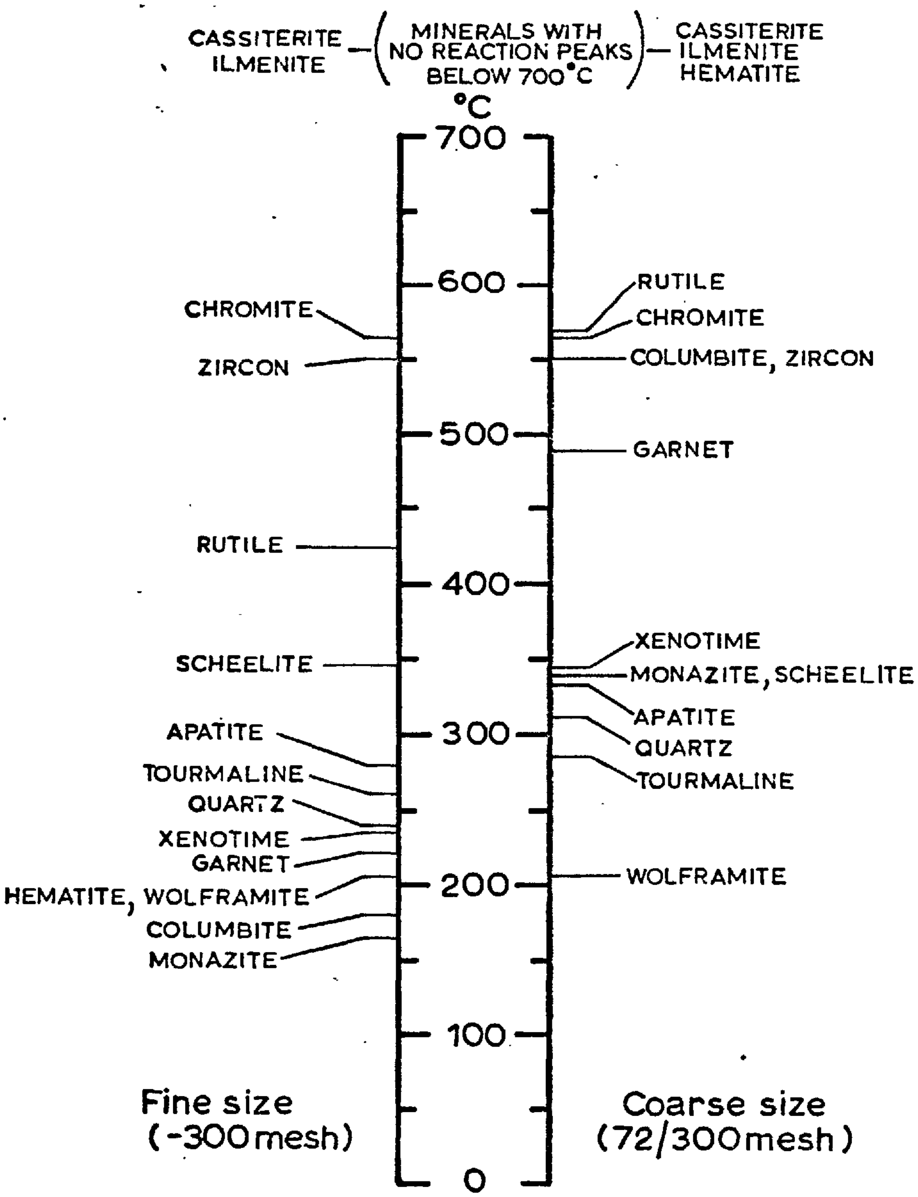


Fig. 8 The reactivities of minerals with sodium hydroxide arranged according to the reaction peak temperatures from the D.T.A. curves obtained.

# PART II

## A DETAILED STUDY OF MONAZITE REACTION

### 1. Introduction

In a reaction of a refractory mineral with sodium hydroxide one would normally expect the resulting products of reaction in a fused mass. Nevertheless the finding from the treatment of zircon(11)(12) suggests that it is not always the case; a mineral could be processed by the reagent without rendering the product in a fused state. In other words the main disadvantages of the conventional fusion process could be eliminated at the same time. These suggestions have been tested thoroughly by experimental methods.

The preliminary reactivity study by D.T.A. indicated the interesting phenomenon that a number of minerals react at much lower temperatures than would normally be expected. Monazite, for example, showed two reaction regions below the melting point of sodium hydroxide. With monazite, however, it has been pointed out (3)(10) that the conventional fusion process yields refractory oxides which dissolve in acids only with difficulty. This appears to be the main reason why the method is not adopted industrially. It is of academic as well as economic interest to study in detail the reaction of this mineral.

The reactivity of monazite has been determined in terms of temperature, time, size of particles and the ratio of sodium hydroxide to mineral. The factors influencing the physical form of the products have been determined. The chemical and physical nature of the products has also been determined by chemical analysis, X-ray diffractometry, optical and electron-probe microscopy and infra-red spectroscopy.

## 2. Experimental Materials

### 2.1 Monazite samples

The monazite sample used for this investigation was obtained from the Han Kuk Monazite Separating Co. Ltd., Korea. Two lots of monazite concentrates were received. The first sample of 5kg was cleaned by magnetic and gravity separation methods and extensively used for the study of reactions. A complete chemical analysis of this cleaned sample (Monazite Sample A) is shown in Table 5. The second sample was 20kg of commercial concentrate (Monazite Sample B) and it was used as received for large scale tests. Table 6 shows the size distribution of the two samples.

In order to obtain information on the mode of element distribution a polished section was examined by an electron probe micro-analyser, by Dr. J. Gavrilovic of the Mineral Technology Department. The result showed that the content of cerium, thorium, lanthanum and neodymium varied (approximately ± 10 – 20% relative) within individual particles as well as from one particle to another, but the content of phosphorus hardly varied. Mineralogical examination of the sample indicated the presence of some impurity minerals such as garnets, tourmaline, zircon and ilmenite. It was found by grain counting of the 72/100 mesh fraction that the total impurity content was approximately 6%.

In order to compare the test results with monazite of different origin, various commercial concentrates were obtained through Mr. I. C. Schomburgk, National Research Development Corporation, London, S.W.1. They were Australian, Ceylonese, Congolese, Indonesian, Korean (C), Malayan, Nigerian and Venetian origin.

Table 5. Chemical analysis on Korean Monazite Sample A

| | |
|---|---|
| $Ce_2O_3$ | 27.8 |
| $La_2O_3$ | 13.0 |
| $Nd_2O_3$ | 11.8 |
| $ThO_2$ | 5.6 |
| $Y_2O_3$ | 2.9 |
| $P_2O_5$ | 26.8 |
| $SiO_2$ | 2.9 |
| $Fe_2O_3$ | 1.7 |
| CaO | 0.8 |
| $TiO_2$ | 0.6 |
| $Al_2O_3$ | 0.4 |
| Total* | 94.3% |

* Also present in low concentrations
Zr, U, Pb, Yb, Ho, Gd, Dy, Er, Sm and Pr.

Assay by Messrs. N.L.Andrew, F.A.Staff, J.Mills and A.C.Lobo, Analytical Services Laboratory, Imperial College.

Table 6. Screen analysis of Korean monazite samples

| Mesh (B.S.) | Sample A. | | Sample B. | |
|---|---|---|---|---|
| | Wt. % | Cum. Wt. % | Wt. % | Cum. Wt. % |
| +36 | 0.0 | 0.0 | 0.0 | 0.0 |
| +52 | 0.0 | 0.0 | 1.5 | 1.5 |
| +72 | 0.7 | 0.7 | 26.4 | 27.9 |
| +100 | 17.9 | 18.6 | 49.6 | 77.5 |
| +150 | 67.7 | 86.3 | 20.6 | 98.1 |
| +200 | 11.9 | 98.2 | 1.8 | 99.9 |
| -200 | 1.8 | | 0.1 | |
| Total | 100.0 | | 100.0 | |

## 2.2 Other Materials

Sodium hydroxide : ANALAR sodium hydroxide pellets from Hopkin and Williams Ltd., were ground in a dry porcelain ball mill with porcelain balls for 2 hours. All possible care in handling the chemical during and after grinding was taken to avoid contamination from the atmospheric moisture and carbon dioxide. The ball mill was flushed with nitrogen before grinding. The finely ground sodium hydroxide was stored in a gas-tight bottle and used for small scale reaction tests. Commercial flakes were ground in separate batches and used for the large scale tests.

Other Chemicals : The other chemicals used in this study were of ANALAR grade reagents unless otherwise specified.

# 3. Experimental Methods

## 3.1 Heat-treatment of sample mixture

The monazite-sodium hydroxide mixture was prepared by mixing the weighed materials in a screw-capped glass bottle (60ml) containing three porcelain balls. An intimate mixture was obtained by means of rolling and gently shaking the bottle.

The mixture was transferred to a silver crucible (35ml) and a chromel-alumel thermocouple was inserted in the centre of the sample. The crucible was hung in a preheated vertical tube furnace. The temperature variation of the furnace was within ± 1°C. The open end of the furnace tube was loosely closed during heating by a piece of asbestos cloth and a small piece of light brick. The temperature of the sample was recorded on a chart recorder during heating period. The arrangement of the equipment is shown in Fig. 9. At the end of the heating period the crucible was cooled in a desiccator to determine the dry weight of the reaction product.

## 3.2 Water-leaching of the reaction product

The reaction product of monazite with sodium hydroxide was leached with water in order to dissolve all the soluble portion of the product. Approximately 5g of dry products were transferred to a 80ml centrifuge tube and hot water (60°C) was poured in with manual agitation.

The reaction mass dissolved readily in cold water, but hot water was used to ensure complete dissolution. After 15 minutes the suspension was centrifuged for 5 minutes at 2000r.p.m. The supernatant solution was decanted into a flask. This operation was repeated twice. For the third washing 0.1 N sodium hydroxide solution was used to maintain the alkalinity of the solution, since the suspension became stable as the number of

Fig. 9 Apparatus for heat-treatment.

washings increased. Washing three times ensured complete dissolution of the soluble phosphorus present in the reaction product. It was experimentally found that 91% of the soluble phosphorus was recovered in the first supernatant solution. The second washing brought nearly complete washing (99%). Also, it was found that only one washing was necessary when 20ml of water was used for every gram of the reaction products. All the leach solutions were collected in a volumetric flask for the determination of phosphorus. The phosphorus in solution was determined and used in calculating the percentage of reaction.

## 3.3 Acid-leaching of the Precipitated oxides

The residue from water leaching, which contained the thorium and rare earth oxides, was leached with hydrochloric, sulphuric or nitric acid. The leaching was carried out in a 250ml round-bottom flask fitted with two reflux condensers. The flask was immersed in a glycerol bath kept at a constant temperature. Both the bath and the contents of the flask were agitated and heated by means of a combined magnetic stirrer and hotplate. The general arrangements are shown in Fig. 10.

Normally 4g of the oxides to 120ml of an acid solution were used for the reaction rate tests. Solution samples of 5ml were taken at suitable time intervals. In order to minimize sampling error, the stirring was stopped for one minute to settle most of the particles and then a little more than 5ml of the solution was taken into a glass tube immersed in cold water. When it was cooled to 20°C exactly 5ml of the solution was transferred into a small frit glass funnel mounted in a suction apparatus, under which the filtrate and washings were received in a 25ml volumetric flask. Filtration was necessary to remove the small quantity of gelatinous matter.

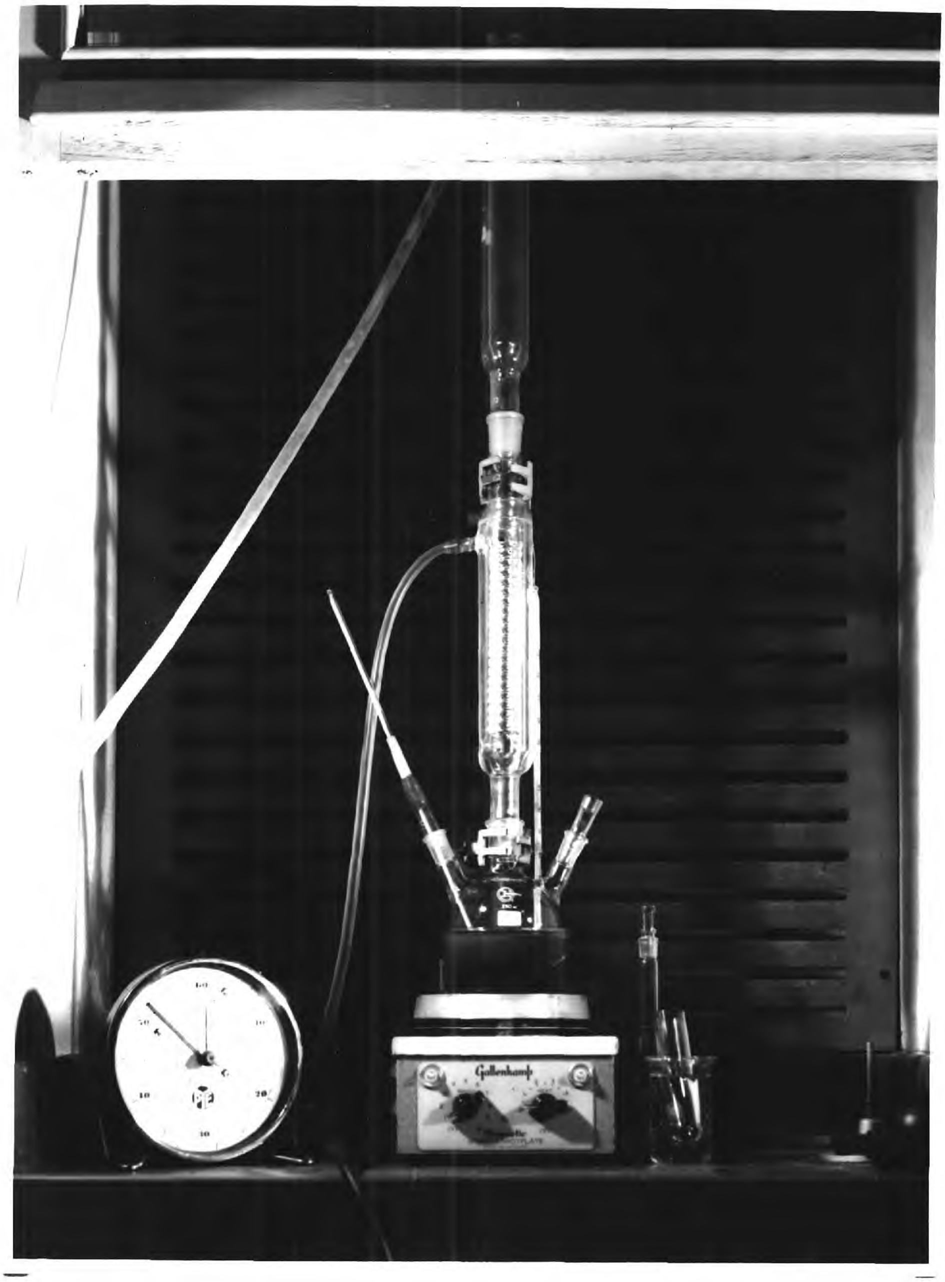


Fig. 10 Apparatus for acid leaching.

The remainder of the sample solution was returned to the reaction vessel without delay.

From 4 to 6 samples were taken for each test run and sent for assay.

## 3.4 Differential leaching

The differential leaching carried out with monazite reaction products comprised selective dissolution of unreacted sodium hydroxide, sodium phosphate and rare earth oxides successively in absolute alcohol, water and hydrochloric acid. In this way it was possible to separate the reaction products into the above mentioned three materials plus unreacted sands.

The crushed dry sample as much as 5g, was first mixed in a 100ml conical flask with 50ml of absolute alcohol for 30min. by means of mechanical shaker. The suspension was centrifuged and the solid was redispersed with alcohol in the tube and recentrifuged. The supernatant solution collected in a 1 litre volumetric flask was diluted to the mark with water and the quantity of sodium hydroxide was determined by acid titration and flame photometry. The residue after centrifuging was dried in a vacuum desiccator over night. The weighed solid residue after the alcohol leach was dissolved in water as described in Section 3.2. The supernatant solution was analysed for phosphorus and sodium. The weighed, dry, residue after alcohol and water leach was dispersed in hot 8 N hydrochloric acid which dissolved only the rare earth oxides leaving behind the original mineral unattacked. Previous dissolution tests showed that no appreciable dissolution of monazite was observed with 8 N hydrochloric acid at 60°C within a few minutes.

The dry weight of each product separated was also calculated by the loss in weight at each stage of leaching.

## 3.5 Infra-red spectroscopy

In order to identify the fritting product of monazite infra-red absorption measurements were carried out using a Grubb Parsons Spectromaster.

Potassium bromide discs were prepared from the monazite reaction products and standards according to the method suggested by Stanfield et. al (18) as follows:
Approximately 2mg of dry sample and 200mg of dry potassium bromide were mixed and ground in a miniature agate ball mill, 15mm x 28mm, mounted in a Grindex shaking machine. The well mixed sample was placed in a cylindrical die, 15mm in inner diameter, and 30tons/in$^2$ of pressure was applied slowly under vacuum. After 3 or 4 minutes the vacuum was released slowly. The thin discs were kept in a desiccator over phosphorus pentoxide.

The spectra for the sample and the standards were recorded over the range of wavelength between 4µm and 25µm using a scan speed of 2µm/min. and 1µm/min.

## 3.6 X-ray diffractometry

X-ray diffractometry was used mainly for identification of monazite and the rare earth products. Debye - Scherrer powder patterns were obtained with a camera of 9cm diameter. The d-spacings were read directly from the film by means of a graduated overlay, and the intensities were estimated. The interpretation was made by reference to the A.S.T.M. Index.(19)

## 3.7 Analytical Methods for phosphorus, sodium and rare earth elements.

### 3.7.1 Phosphorus

The phosphorus content in solution was determined by a gravimetric method similar to that described in the literature.(20) The method employs precipitation of phosphorus in nitric acid solution as ammonium phosphomolybdate $[(NH_4)_3PO_4.12MoO_3.2HNO_3]$ by addition of an excess of ammonium molybdate solution. An appropriate volume of the sample solution was acidified with nitric acid, heated to 40°C, and ammonium molybdate solution added in excess (>2ml/mg P). After warming for 1 hour at the temperature, it was filtered on No.4 sintered glass crucible and the precipitate was washed with dilute nitric acid solution. Phosphorus was determined from the dry weight of the precipitate (110° - 120°C for 1 hr) by multiplying by 0.0165.

### 3.7.2 Sodium

Sodium was determined by flame photometry. The equipment used was an 'EEL' Flame Photometer Mark II. The sample solution was atomised into a mixing chamber where it was mixed with air and fuel gas and ignited in the burner. The concentration of sodium was obtained from a calibration curve. The standard solutions were prepared from ANALAR grade disodium hydrogen orthophosphate in the concentration range from 1 to 50 mg/100ml. No interference was observed with Ce, $NO_3^-$, and alcohol which were the main constituents other than Na and P.

### 3.7.3 Rare earth element and thorium

An X-ray fluorescence analytical method was employed for the determination of the rare earth elements and thorium, which was carried out by Mr N. Andrews and Mr J. Mills, Analytical Services Laboratory, Imperial College.

The equipment used was a Philips PW 1220 Semi-automatic X-Ray Fluorescence Spectrometer, with associated recording equipment. The radiation detectors were (i) scintillation counter and (ii) gas flow proportional counter (90% argon and 10% methane gas mixture).

The samples, which were solutions derived from monazite or the products of reaction of monazite, were analysed for Ce, La, Nd, and Th. Synthetic standard solutions, containing a range of known concentrations of these four elements, were prepared from ANALAR grade thorium nitrate, ammonium ceric nitrate, and reagent grade lanthanum and neodymium nitrates. An internal standard solution was made to contain Sr, Cr and Ti in dilute nitric acid. The solution for analysis was prepared by mixing 10ml of standard or sample solution, 1ml of concentrated nitric acid, and 5ml of internal standard solution. Concentrated nitric acid was added with shaking to dissolve any precipitate formed during mixing. The samples were analysed in air-path conditions, the solutions during analysis were contained in polythene cups with 6μ Mylar windows; about 15ml of solution were required. In all cases, the analysing crystal was LiF <200>. The samples were spun during counting at a rate of 6 r.p.m.

Background counts were taken on both sides of every peak, and the calculated mean values of background at both peak positions were subtracted from the peak counts to give a net peak intensity. Calibration graphs were drawn for each of the four elements determined, and within each of the two sets of samples, by plotting concentration of the standard solutions against the net peak intensity ratio, unknown : internal standard.

# 4. Experimental Results and Discussion

## 4.1 Products of reaction

The reaction products of monazite were identified by chemical analysis, x-ray diffraction and infra-red spectroscopy. In the first part of this Chapter the results obtained by the above methods will be described. A summary of the findings will be given at the end together with a set of chemical equations describing the stoichiometry of the overall reactions.

### 4.1.1 Products from differential leaching

The products of reaction of monazite with sodium hydroxide separated into four categories in the following order: (i) alcohol-soluble, (ii) water soluble, (iii) acid-soluble, and (iv) acid insoluble materials. The main products of this separation scheme were: (i) unreacted sodium hydroxide in the alcohol-soluble fraction, (ii) sodium phosphate and sodium hydroxide produced by hydrolysis in the water-soluble fraction, (iii) rare earth oxides in the acid soluble fraction and (iv) unreacted mineral. The amount of sodium carbonate incidentally formed was separately determined by measuring in a gas burette the volume of carbon dioxide evolved when excess acid was added to the whole products. Two series of reaction products obtained from mixtures containing various proportions of sodium hydroxide after heating to two different temperatures (200°C, 360°C) were differentially leached.

The mass distribution of the each product and of the principal elements (Na, P and Ce) are shown in Table 7. Some of the results are shown graphically in Figs. 11 and 12. The percentage of extraction expressed in Fig. 11 refers to the mineral for phosphate and oxides, and to the initial quantity of NaOH in the mixture for unreacted sodium hydroxide. It can be seen from Fig. 11 that the unreacted sodium hydroxide

Table 7 Results of differential leaching of Monazite reaction products

| Test No | Initial wt. ratio mixed | Description | | separated | | Products | | |
|---|---|---|---|---|---|---|---|---|
| | | | | (excess NaOH) | (Sod. Phosphate) | (Oxides) | (Unreacted sands) | Total % |
| 1 | $\frac{NaOH}{Monazite} = 0.15$ | Product, wt.% | | 0.59 | 15.50 | 17.57 | 66.36 | 100.0 |
| | | Element distribution % | Na | 6.5 | 90.8 | - | - | 97.3 |
| | | | P | 0.0 | 23.3 | 0.0 | (76.7) | (100.0) |
| | | | Ce | 0.0 | 0.1 | 25.7 | (74.2) | (100.0) |
| 2 | $\frac{NaOH}{Monazite} = 0.30$ | Product, wt.% | | 0.97 | 26.89 | 28.25 | 43.89 | 100.0 |
| | | Element distribution % | Na | 7.2 | 92.0 | - | - | 99.1 |
| | | | P | 0.0 | 44.6 | 0.0 | (55.4) | (100.0) |
| | | | Ce | 0.0 | 0.1 | 48.3 | (51.6) | (100.0) |
| 3 | $\frac{NaOH}{Monazite} = 0.60$ | Product, wt.% | | 4.89 | 40.13 | 39.83 | 15.15 | 100.0 |
| | | Element distribution % | Na | 14.6 | 82.2 | - | - | 96.8 |
| | | | P | 0.0 | 77.2 | 0.0 | (22.8) | (100.0) |
| | | | Ce | 0.0 | 0.1 | 79.7 | (20.2) | (100.0) |
| 4 | $\frac{NaOH}{Monazite} = 0.75$ | Product, wt.% | | 5.67 | 46.90 | 41.69 | 5.74 | 100.0 |
| | | Element distribution % | Na | 22.3 | 79.1 | - | - | 101.4 |
| | | | P | 0.0 | 91.8 | 0.0 | (8.2) | (100.0) |
| | | | Ce | 0.0 | 0.1 | 91.1 | (8.8) | (100.0) |
| 5 | $\frac{NaOH}{Monazite} = 0.90$ | Product, wt.% | | 10.41 | 45.98 | 39.93 | 3.48 | 99.8 |
| | | Element distribution % | Na | 28.8 | 69.6 | - | - | 98.4 |
| | | | P | 0.0 | 96.3 | - | (3.7) | (100.0) |
| | | | Ce | 0.0 | 0.1 | 96.9 | (3.0) | (100.0) |
| 6 | $\frac{NaOH}{Monazite} = 1.05$ | Product, wt.% | | 15.62 | 44.38 | 37.61 | 2.38 | 99.9 |
| | | Element distribution % | Na | 34.7 | 60.2 | - | - | 94.9 |
| | | | P | 0.0 | 99.2 | 0.0 | (0.8) | (100.0) |
| | | | Ce | 0.0 | 0.1 | 97.5 | (2.4) | (100.0) |

— undetermined; ( ) estimated by subtraction

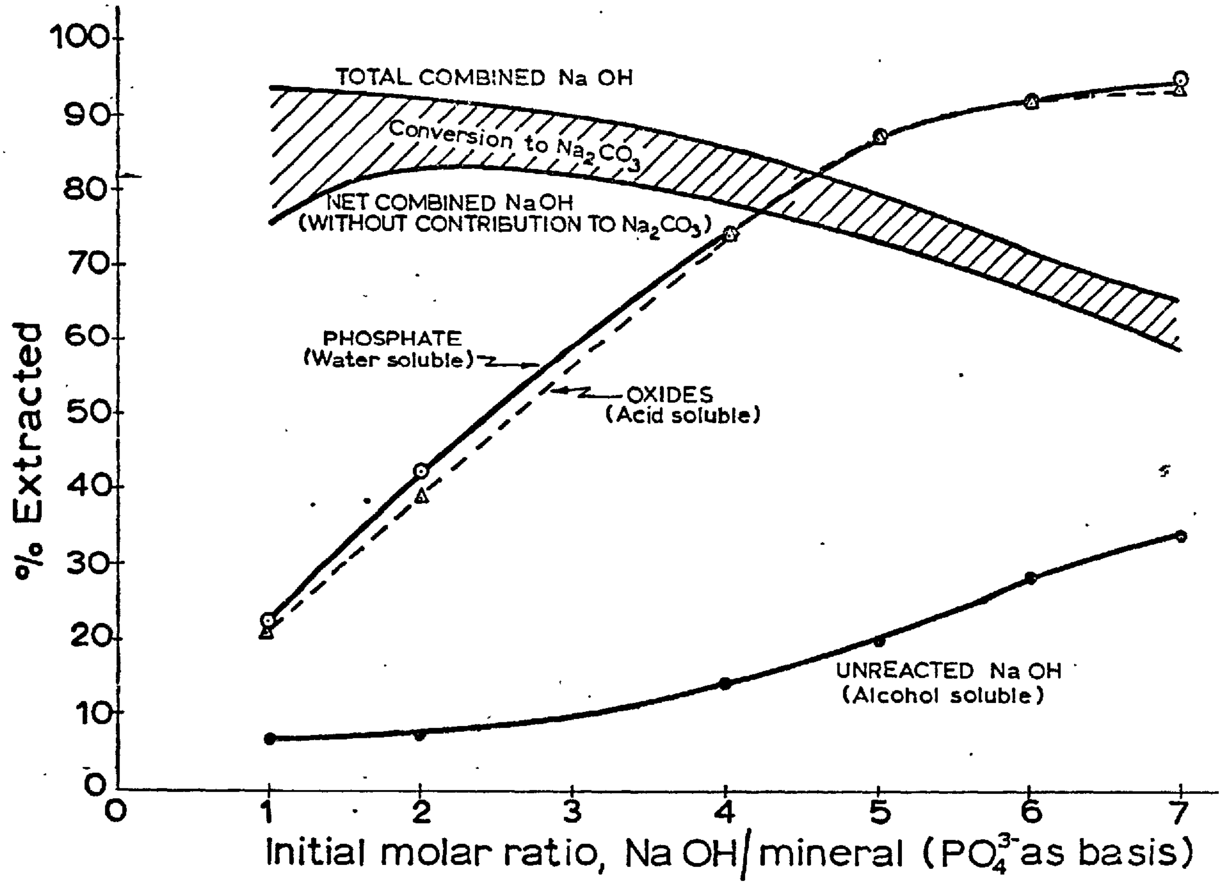


Fig.11 Results of differential leaching of reaction products obtained from various Na OH/monazite molar mixtures heated to 360 °C for 1 hour.

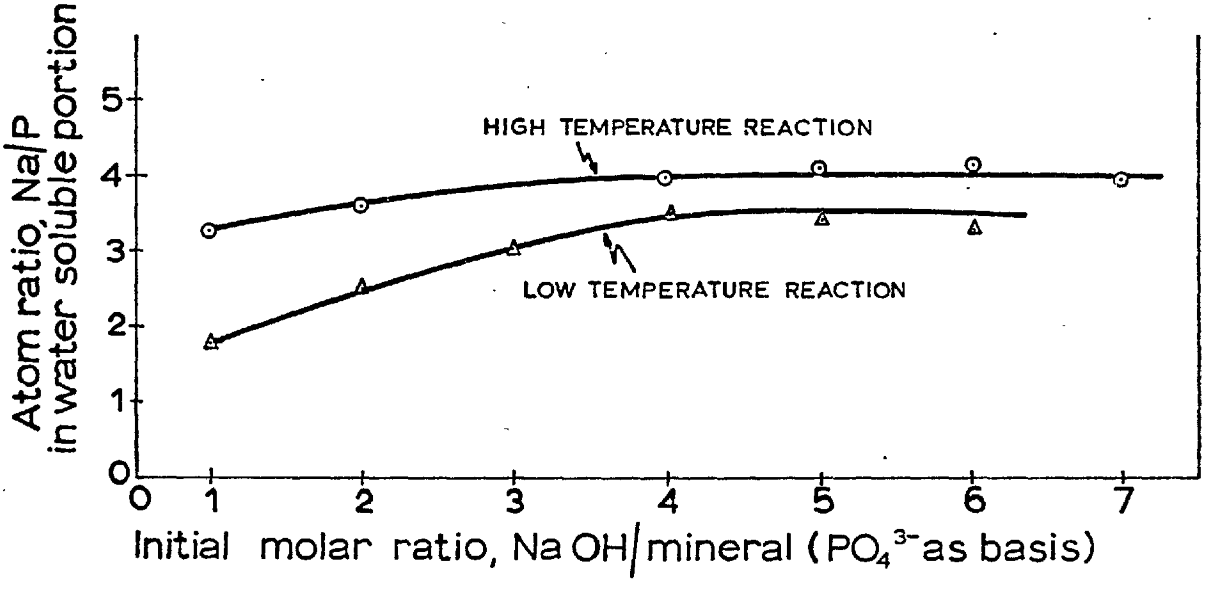


Fig. 12 Atom ratio Na/P in water soluble portion of differential leaching.

ranged from 7% to 34% in the range of initial molar ratio from 1 to 7. The combined sodium hydroxide represents that quantity of sodium hydroxide which was in the form of sodium compounds other than sodium carbonate. This quantity was obtained by subtraction of the unreacted sodium hydroxide and sodium carbonate from the initial quantity of sodium hydroxide added.

The curves for solubilized phpsphate and oxides nearly coincided together indicating that each is a sound measure of the extent of decomposition of the monazite.

The atom ratios, Na/P, in the water soluble portion of the reaction products are shown (Fig. 12) for the two series of products obtained at the two temperatures.

The sodium in the calculation of the atom ratios was that derived from sodium compounds other than sodium carbonate. From the figure it can be seen that the ratio for the high temperature reaction was higher than that for the low temperature reaction. In both cases the atom ratios are lower when NaOH was deffficient and gradually increased to an average value of 4.0 for the high temperature reaction and 3.5 for the low temperature reaction. When the initial NaOH : mineral ratio was greater than 4.0 the Na/P atom ratios of the products were constant.

The monazite solubilized was directly proportional to the net sodium hydroxide consumed (excluding sodium carbonate), as shown in Figs. 13 and 14 respectively for the high and low temperature products. From the slopes of the lines it was calculated that the net molar ratio, $NaOH/[PO_4]$, for the high temperature reaction was 4.4 and that for the low temperature reaction was 3.45. Although the net alkali consumption is expressed in terms of the phosphate content it is not assumed that sodium phosphate is the only sodium compound derived from

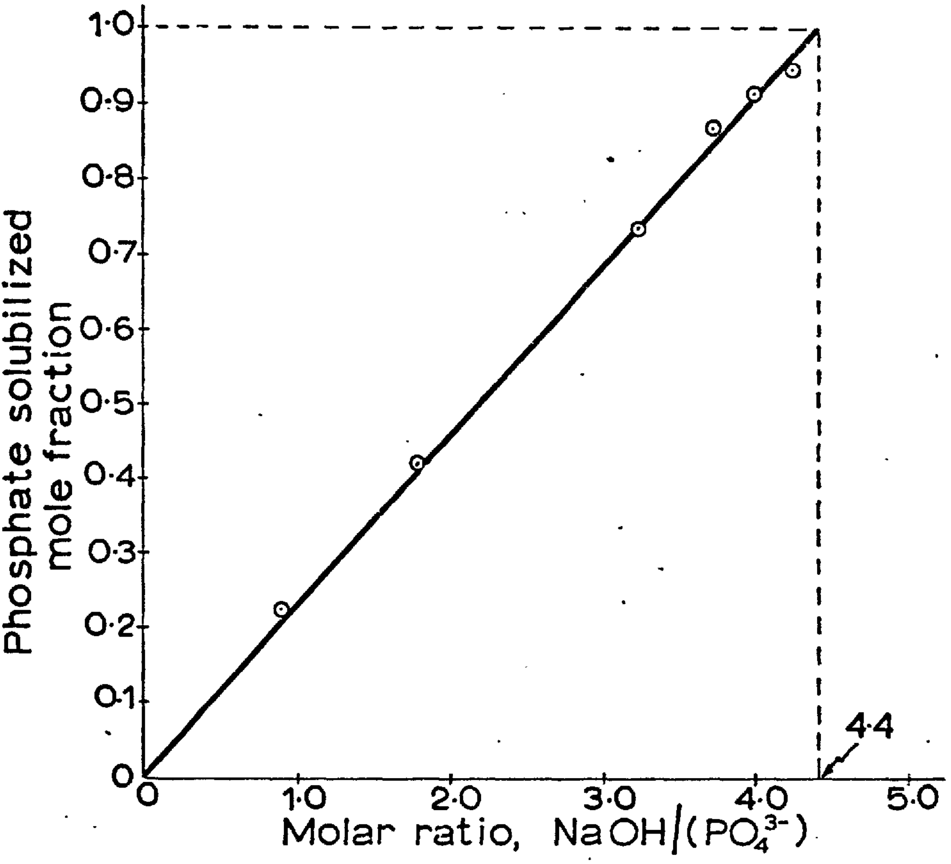


Fig. 13 Relationship between monazite solubilized and sodium hydroxide consumed at 360°C. (Coarse monazite)

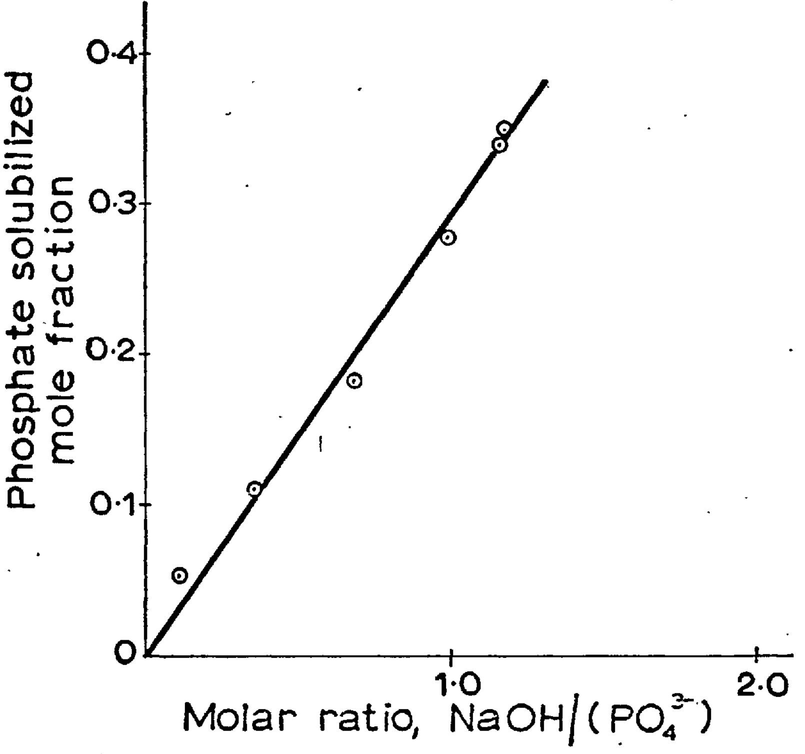


Fig.14 Relationship between monazite solubilized and sodium hydroxide consumed at 200°C. (Fine size monazite)

the mineral. This point will be discussed later (PART II 4.1.4) in the light of further evidence.

### 4.1.2 X-ray diffraction patterns of the reaction products

Debye - Scherrer powder patterns were obtained for the various reaction products of monazite. The lines in the film were diffuse and some of them were faint that it was not possible to measure the d-spacings accurately. However, the measurable lines were compared with available A.S.T.M. Index(19) or artificially prepared materials. The results of the observations are summarized in Table 8.

It was almost impossible to identify sodium compounds even though considerable quantities of sodium hydroxide and sodium phosphate were present in the sample. All the lines of the sodium phases were faint and almost indistinguishable because of the scattering action of the heavy atoms present. An X-ray powder pattern of a synthetic 50% molar mixture of $CeO_2$ and $Na_3PO_4$ showed that the lines corresponding to $CeO_2$ were strong whereas the lines corresponding to $Na_3PO_4$ were only faint. The intensity of the strongest line of $Na_3PO_4$ was much weaker than the weakest line (5%) of $CeO_2$ and was less than 10% that obtained in the absence of $CeO_2$. Although some faint lines corresponding to $Na_3PO_4$ and NaOH were detected in some samples it was clear that this method was inadequate for identifying the sodium compounds.

As indicated in the Table 8 the lines for individual rare earths and thorium oxides (or hydroxides) were missing in almost all of the products even after treatment by water. The patterns of the products indicated a phase not reported in the A.S.T.M. Index. All the distinguishable strong lines corresponded to a phase which had similar structure to sodium chloride; the lattice constant varied in a range of

Table 8 Interpretation of X-ray patterns obtained from various products of monazite

| Sample No. | A111 | A109 | A113 | A115 | A112 | A111R | A112R | UFA | A111RH | A111RN |
|---|---|---|---|---|---|---|---|---|---|---|
| Description of treatment:- wt.ratio of monazite: NaOH<br>Temp.<br>Time, etc. | Heated product of 1:1 mix<br>360°C<br>3 hr | Heated product of 1:1 mix<br>360°C<br>0.5 hr | Heated product of 1:0.15 mix<br>360°C<br>1 hr | Heated product of 1:0.15 mix (-300 mesh)<br>360°C<br>1 hr | Heated product of 1:1 mix (-300 mesh)<br>200°C<br>0.5 hr | Water leach residues of A111<br>(oxides) | Water leach residues of A112<br>(Oxides) | Alcohol leach residues of A111 | HCl leach residues of A111R<br>(sands) | $HNO_3$ leach residues of A111R<br>(sands) |
| $CeO_2$ | X | X | X | X | ? | X | X | X | X | X |
| $La_2O_3$ | X | X | X | X | X | X | X | X | X | X |
| $La(OH)_3$ | X | X | X | X | ? | X | X | X | X | X |
| $Nd_2O_3$ | X | X | X | X | X | X | X | X | X | X |
| $Nd(OH)_3$ | X | X | X | X | X | X | X | X | X | X |
| $ThO_2$ | X | X | X | X | X | X | X | X | X | X |
| $NaH_2PO_4$ | X | X | X | X | ? | X | X | X | X | X |
| $Na_2HPO_4$ | X | X | X | X | X | X | X | X | X | X |
| $Na_3PO_4$ | ? | ? | ? | ? | ? | X | X | O | X | X |
| NaOH | X | ? | X | O | X | X | X | X | X | X |
| $NaPO_3$(I) | X | X | X | X | X | X | X | X | X | X |
| $NaPO_3$(II) | X | X | X | X | X | X | X | X | X | X |
| $Na_2CO_3$ | X | X | X | X | X | X | X | X | X | X |
| $2CeO_2.Y_2O_3$ | X | X | X | ? | X | X | X | X | X | X |
| monazite | ? | ? | ? | O | O | O | O | ? | O | ? |
| ilmenite | O | O | O | X | ? | O | X | X | O | O |
| anorthite | X | X | X | X | X | X | X | X | X | X |
| gehlenite<br>(Ca-Al-silicate) | X | X | X | X | X | ? | X | X | ? | X |
| zircon | X | X | X | X | ? | ? | ? | X | O | O |
| New phase Cubic; NaCl Structure. ( $a_o$ ) | O<br>5.54Å) | O<br>(5.54Å) | O<br>(diffused)<br>(5.57Å) | ?<br>- | ?<br>- | O<br>(5.51Å) | ?<br>- | O<br>(5.52Å) | X<br>- | O<br>(5.49Å) |

Note:

O : Possibly present
? : Doubtful (some lines match but are not distinct)
X : Not present or lines are unidentifiable

$a_o$ = 5.49 to 5.57Å. The heated product with 1:1 weight ratio of monazite and sodium hydroxide had $a_o$ = 5.54Å whereas in the product incompletely leached by acid $a_o$ = 5.49Å. The material reported in the A.S.T.M. Index which gave the closest fit to the observed diffraction was a solid solution of $CeO_2$ (75%) and $ThO_2$(25%) in the same crystal structure (NaCl) with $a_o$ = 5.47Å.

From the chemical fact that

(i) the heated product contained Th, Ce, and other rare earth elements together with sodium hydroxide;

(ii) the water leach solution from the heated products (without free NaOH) contained excess sodium than that of contribution from $Na_3PO_4$ and $Na_2CO_3$; and together with the structural information that

(iii) the lines for individual compounds, such as $CeO_2$, $La_2O_3$, $Nd_2O_3$, $ThO_2$ etc., were missing in the pattern except, though with considerable uncertainty, that of the low temperature products, the new phase formed was probably a solid solution of these oxides in which sodium was also associated, which may be generally expressed as

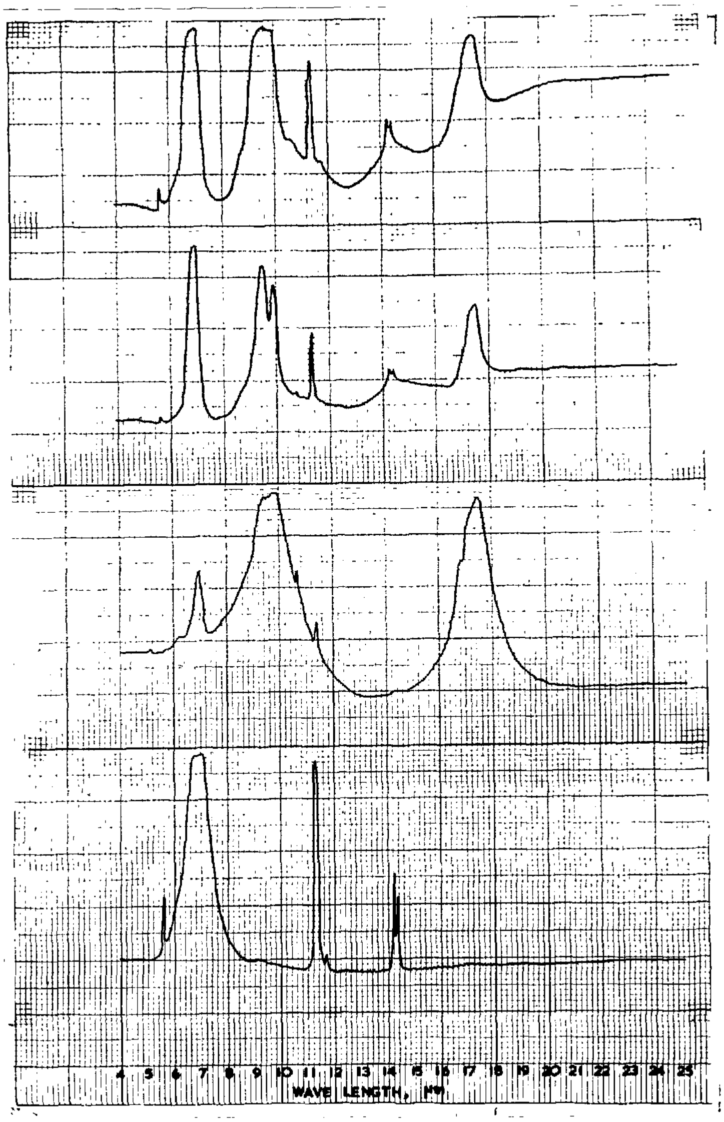
$$xNa_2O.y\ R_2^{III}O_3.zR^{IV}O_2$$

Where $R^{III}$: La, Nd, etc., $R^{IV}$ : Ce, Th.

The unit cell constant of the phase became smaller in the successive products of leaching by alcohol, water, and acid from 5.54Å to 5.49Å. The contraction of the lattice was presumably caused by the removal of sodium atoms.

### 4.1.3 Infra-red absorption spectra

For the purpose of identifying phosphate phases present in the reaction products of monazite, infra-red absorption measurements were made and compared with known standards. Some of the recorded spectra are shown in Fig. 15. As is



(a)

Reaction product of monazite and NaOH obtained by heating to 360°C.

(b)

Reaction product of monazite and NaOH obtained by heating to 200°C.

(c)

Anhydrous $Na_3PO_4$ obtained by heating dodeca-hydrate to 360°C.

(d)

Anhydrous $Na_2CO_3$ (ANALAR)

Fig. 15 Infra-red absorption spectrographs of the reaction product of monazite and standard materials.

apparent from the figure, the sodium phosphate phase present in the reaction product was tri-sodium orthophosphate ($Na_3PO_4$). The reaction product obtained with fine monazite at 200°C also contained the same phase. Both the low and high temperature reaction products contained no other phosphate phases than this. Some of the absorption bands at wave lengths 6.9, 11.3, 14.2 and 14.4µm suggest that the reaction products of monazite contain some carbonate possibly as $Na_2CO_3$.

### 4.1.4 Summary:- Chemical Equations

The chemical reactions occuring in the mixture of monazite and sodium hydroxide are not simple to formulate in an equation since not only is the mineral composed of many elements of different chemical nature but also because the reaction with sodium hydroxide may be different depending on the temperature and the quantity of sodium hydroxide available. The preliminary study using the D.T.A. method indicated two predominant reactions at two different temperatures. This was also observed by the quantitative reaction tests carried out as a function of temperature. It was therefore, attempted to investigate in more detail the reaction occuring at 200°C and 360°C respectively, and to formulate the chemical reactions. The overall stoichiometric requirement of sodium hydroxide was determined experimentally to be 3.45 and 4.40 moles per mole of mineral respectively for the reactions at the lower and upper temperatures. (See Figs. 13 and 14) The sodium phosphate phase in both reaction products was identified by infra-red spectroscopy, as $Na_3PO_4$ (Part II 4.1.3.), no other sodium phosphate phases were detected in the products. The x-ray diffraction patterns, which were of little use in identifying sodium phosphate phases, indicated formation of a new solid solution which was similar to that of $(Ce,Th)O_2$ phase, but of greater lattice constants (see Table 8).

No appreciable influence on the decomposition of monazite was observed with the reaction under hydrogen flow. (See Fig.16). Only a slight change in colour of the the products (brown to light brown) was noted but the extent of reaction was essentially similar.

The formation of sodium rare earth double oxide compounds ($Na_2CeO_3$, $Na\ LaO_2$) has been reported(21)(22). It has also been reported that thorium oxide ($ThO_2$) does not react with sodium hydroxide even at a temperature range as high as 850° - 1000°C. (21)

From the information available (summarized in Table 9) the reactions occuring in the mixture of monazite and solid sodium hydroxide at around 350°C may be expressed chemically as follows:

$$2CePO_4 + 10NaOH + \tfrac{1}{2}O_2 = 2Na_3PO_4 + 2Na_2CeO_3 + 5H_2O \quad \ldots \quad (1)$$

$$Th_3(PO_4)_4 + 12NaOH = 4Na_3PO_4 + 3ThO_2 + 6H_2O \quad \ldots \quad (2)$$

$$RPO_4 + 4NaOH = Na_3PO_4 + NaRO_2 + 2H_2O \quad \ldots \quad \ldots \quad (3)$$

Where R represents trivalent elements such as La, Nd, Y, etc. For the low temperature reactions the following equations are probably more realistic:-

$$CePO_4 + 3NaOH + \tfrac{1}{4}O_2 = Na_3PO_4 + CeO_2 + 3/2\ H_2O \quad \ldots \quad (4)$$

$$Th_3(PO_4)_4 + 12NaOH = 4Na_3PO_4 + 3ThO_2 + 6H_2O \quad .. \quad (2)$$

$$2RPO_4 + 6NaOH = 2Na_3PO_4 + R_2O_3 + 3H_2O \quad \ldots \quad (5)$$

The various rare earth compounds in the products, however, would appear structurally to be in the form of a solid solution, $xNa_2O.yR_2O_3.z(Ce,Th)O_2$. The calculation based on the chemical assay results of the monazite and the above equations (1 - 3) gave the stoichiometric quantity required to be a molar ratio, $NaOH/[PO_4] = 4.50$ for the high temperature reaction whereas the

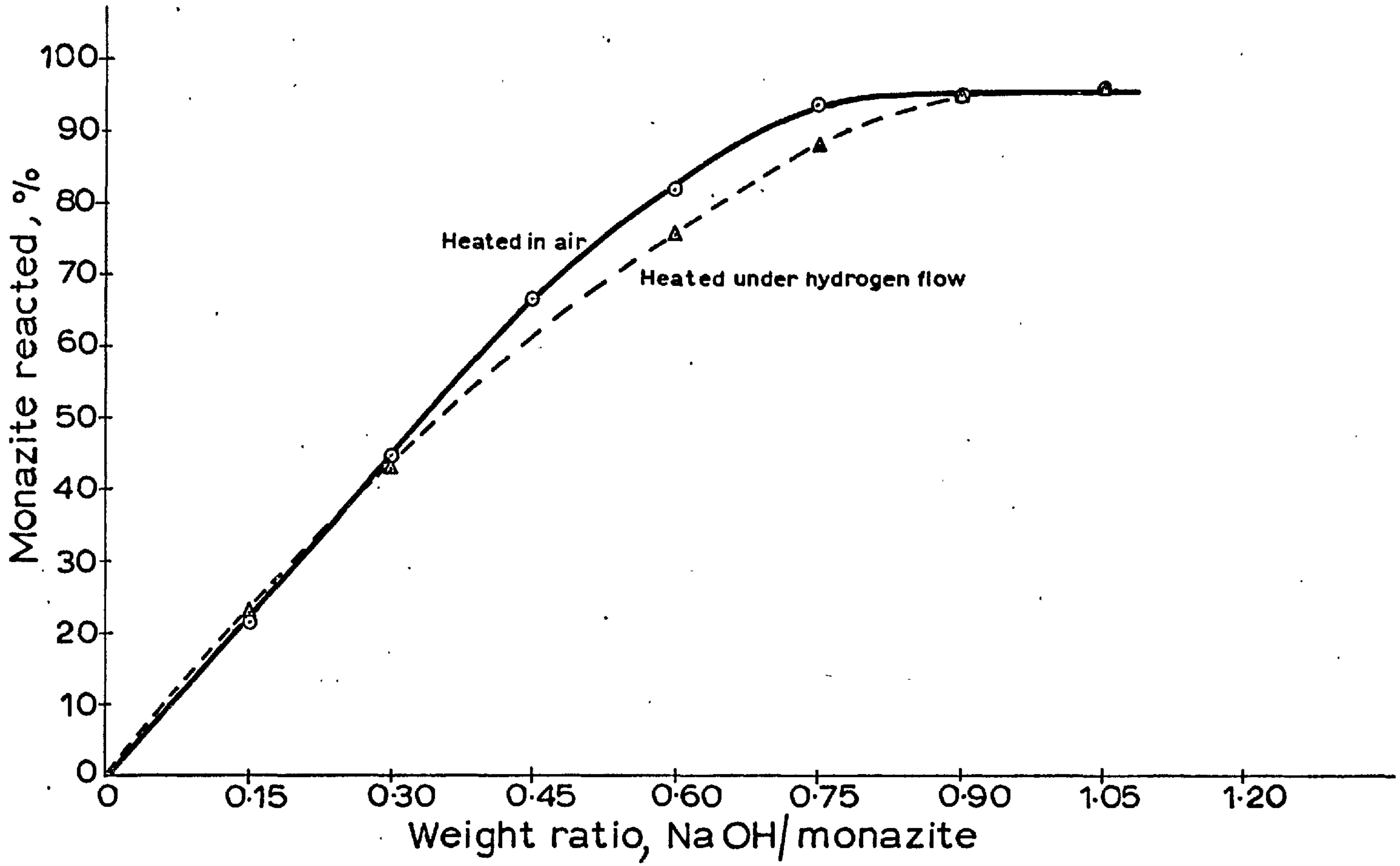


Fig. 16 Reaction of monazite with sodium hydroxide as a function of weight ratio of sodium hydroxide to monazite. (Heating to 360°C for 1 hour)

Table 9 Summary on the Product of monazite and stoichiometry.

| description | Net molar ratio required (without excess NaOH) $NaOH/[PO4^{3-}]$ | Possible Phases in the Product | | | |
|---|---|---|---|---|---|
| | | Phosphate | Rare earths phases | | Na/P atom ratio in aqueous solution |
| | | | Structurely | Individually for rare earths | |
| High temp Reaction (360°C) | 4.40 (exp.)<br>4.50 (calc.) | $Na_3PO4$ | solid solution of Na, rare earths & Th oxides | $Na_2CeO_3$<br>$NaLaO_2$<br>$NaNdO_2$<br>$NaY\ O_2$ | 3.3 – 4.05 (exp.)<br>3.78 (calc.) |
| Low temp Reaction (200°C) | 3.45 (exp.)<br>3.10 (calc.) | $Na_3PO4$ | Solid solution + individual oxides (?) | Partly double oxides partly individual oxides (?) | 1.8 – 3.5 (experimental)<br>3.0 (calculated) |
| Source | Experimental & calculation | Infra-red spectrographs | X-ray powder patterns | References (21) (22) | Experimental & calculation |

experimental determination gave 4.40. The ratios for the low temperature reaction were 3.10 (calculation) and 3.45 (experimental determination). The two values for the high temperature reactions are close together supporting the postulate; however, the values for the low temperature reactions are somewhat apart, suggesting that additional reactions such as (1) and (3) could account for the excess sodium hydroxide consumed.

In view of the fact that the atomic ratios, Na/P, varied as the ratio of sodium hydroxide employed, it should be interpreted that the two sets of equations apply only to the two extremes viz. the equations (1),(2) and (3) for the reactions where high temperature and high ratio of sodium hydroxide are involved and equations (2),(4) and (5) for the reactions where low temperature and low ratio of sodium hydroxide are involved. Equation (2) would apply up to a temperature as high as 1000°C regardless of the ratio of sodium hydroxide. It is therefore possible to obtain any intermediate cases between the two extremes, namely the combination of the equations depending on the temperature and the ratio of sodium hydroxide employed. Nevertheless, it is considered that the two sets of equations proposed to account for the reactions at the two different temperatures would by no means be far from reality.

## 4.2 The rate of reaction

In the aqueous caustic treatment of monazite Bearse et. al. (3) have pointed out that the reaction rate was slow even with fine particles of the mineral (-325 mesh A.S.T.M.). They mentioned that the time taken for complete reaction ranged from 2 to 3 hours at 140°C with the ground monazite.

In the reaction with solid caustic alkali the time for complete reaction with unground monazite sands (see Table 6) was only a few minutes when the solid mixture reached a temperature around 280°C. As the mixture took a finite time to reach the reaction temperature and it could not be readily quenched to stop the reaction after a specified time, it was not possible to determine the relation between extent of reaction and time of reaction. The rate data to be discussed are in the form of extent of reaction after a specified time in the furnace which was preheated to the required temperatures.

The various factors which influence the rate of reaction are discussed in the following sections.

### 4.2.1. The effect of temperature on the extent of reaction

The reaction of monazite with solid sodium hydroxide was investigated as a function of temperature on two size ranges, 72/300 and -300 mesh fractions. An intimate mixture of 5g each of monazite and sodium hydroxide was heated for one hour to various temperatures in the manner described in Section 3.1 (PART II). The percentage of the mineral reacted was obtained by determination of the soluble phosphorus in the water leach solution.

The results are plotted as percentage of reaction against temperature in Fig. 17, from which it can be seen that the fine and coarse size of monazite reacted differently. The coarse monazite reacted at a perceptible rate at around 250°C and the rate (as indicated by the quantity reacted in a fixed time) increased sharply up to about 300°C. Whereas the fine mineral reacted at around 100°C and showed an apparent constant value between 150°C and 260°C, above which a further increase occurred corresponding to the reaction observed with the coarse particles. In other words there were probably two critical reaction temperatures, at around 100°C and 250°C, at which there was a marked increase in the rate of reaction. The rate of reaction of the mixture between the two critical temperatures appears to be

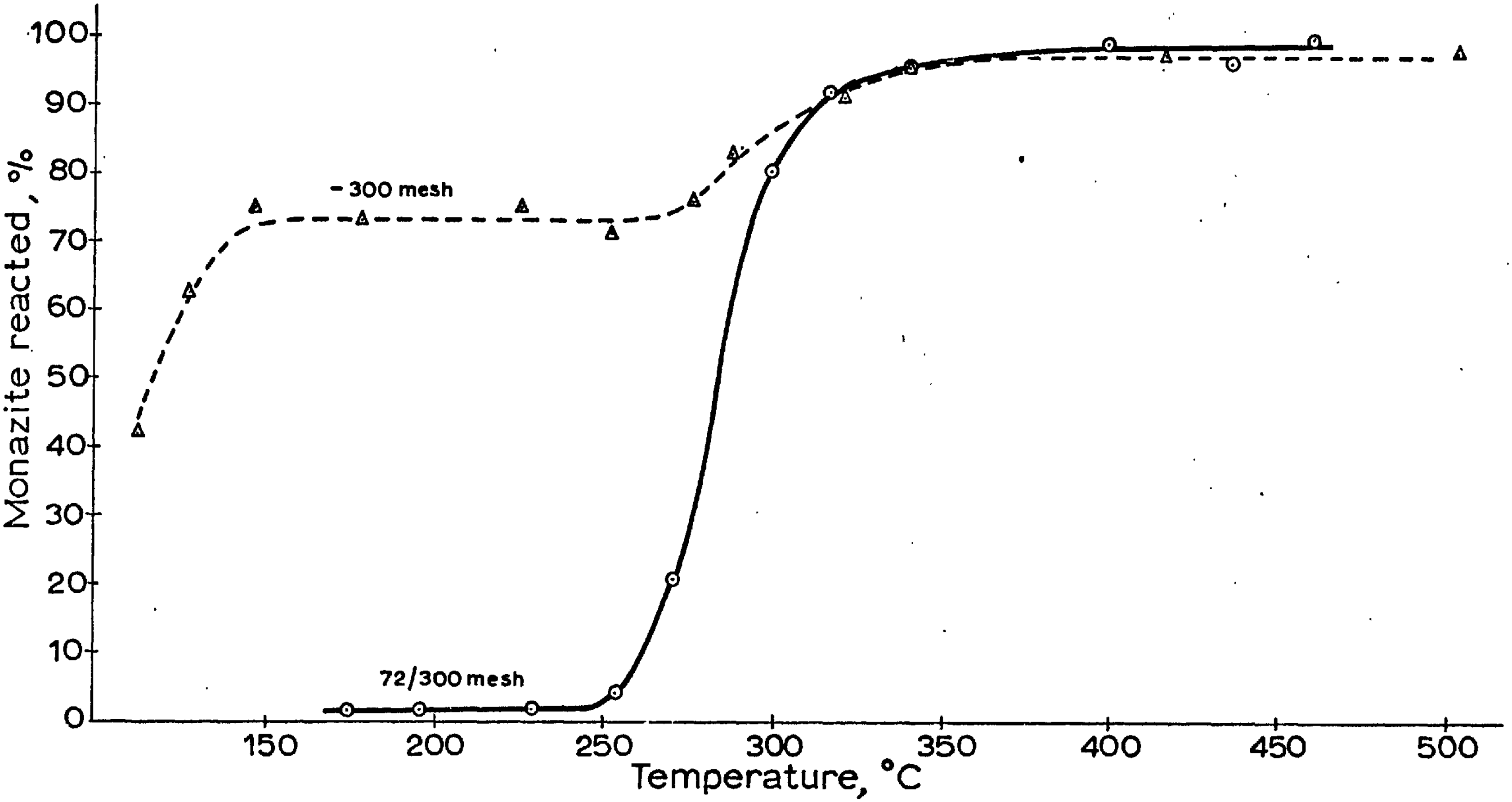


Fig. 17 Reaction of monazite with sodium hydroxide as a function of temperature on two size ranges. Residence time : 1 hour, Weight ratio : Na OH/monazite = 1·0

markedly slower than at the critical temperatures.

### 4.2.2 The progress of the reaction as a function of the residence time.

The effect of heating on the reaction of monazite was investigated with mixtures (1 : 1 by weight) of monazite and sodium hydroxide at 360°C. All the recorded heating curves showed that the exothermic reaction of coarse monazite started as soon as the temperature reached 280°C (see Fig. 18) The time taken to heat the 10g. sample mixture to this temperature was normally less than 10min. The exothermic peak was obtained within a further 5 min., during which time almost complete reaction was achieved. It can be seen from Fig. 20 that the mineral reacted in those periods of time (15 min.) amounted to as much as 90% . In other words the reaction is exceptionally fast above 280°C considering its relative time from the practical reaction at 280°C to the maximum temperature is almost independent of the mass treated. In a test with 1000g of mixture the time taken for this period was only 18 minutes (see Fig. 30).

The heating curves can be divided into the following four characteristic parts (see Fig. 18):

(i) heating period A :- the time for the sample mixture to reach 280°C from room temperature,

(ii) heating period B:- the time from 280°C to the maximum temperature,

(iii) heating period C:- the time from the maximum temperature to the constant equilibrium temperature,

(iv) heating period D:- the holding time at the constant temperature.

The period A is significant in terms of heating the reactants to the temperature of initial reaction. This will

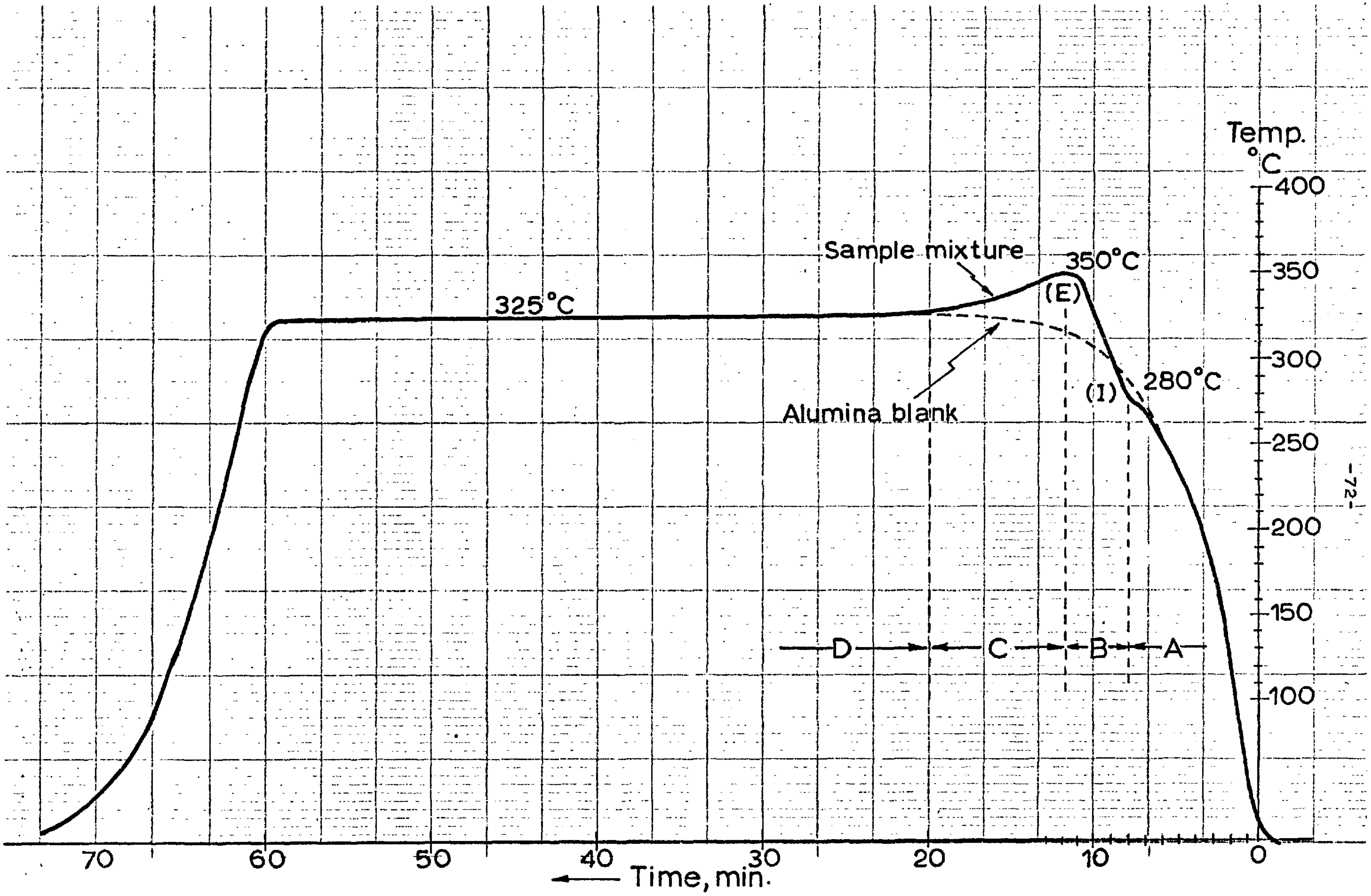


Fig. 18 Heating curve for the mixture of monazite (72/300 mesh) and sodium hydroxide (1:1 by weight)

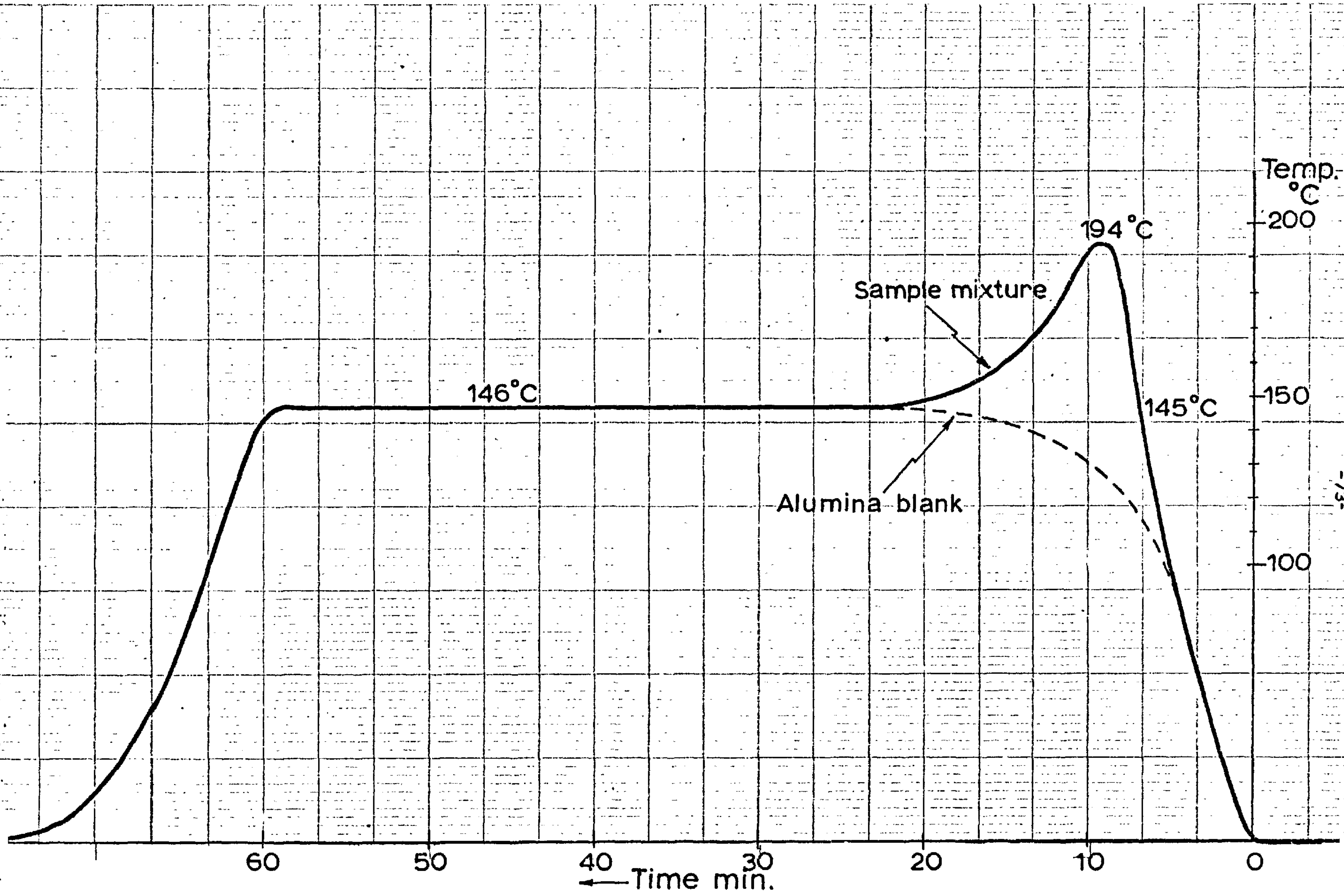


Fig. 19 Heating curve for the mixture of fine monazite (-300 mesh) and sodium hydroxide (1:1 by weight)

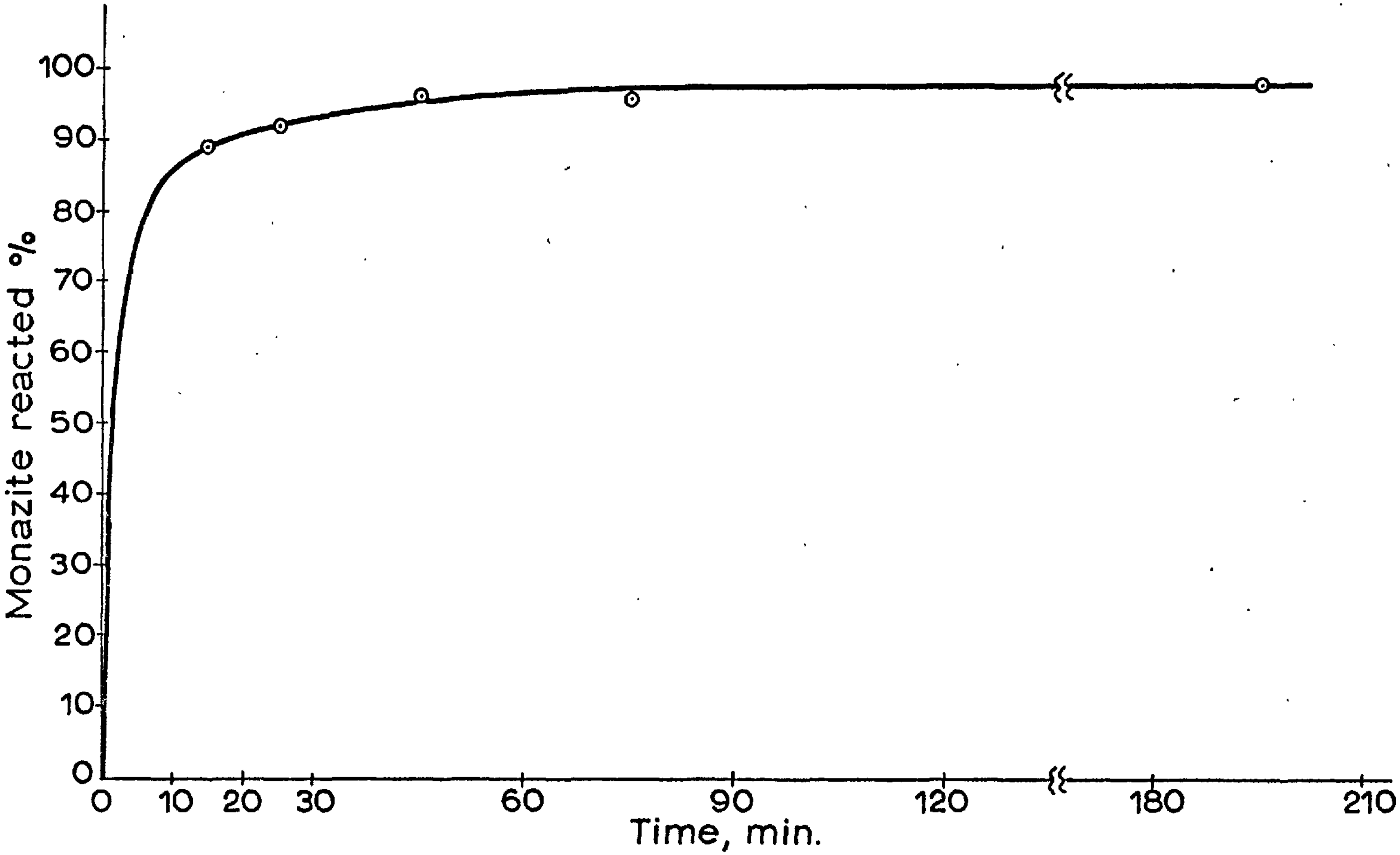


Fig. 20 Reaction of monazite with sodium hydroxide as a function of residence time in the furnace preheated to 360°C. (Weight ratio of NaOH/ monazite = 1·0)

depend on the temperature gradient, the mass and shape of the reactant mixture. It took 8 min. and 10 min. for 10g and 30g of mixture respectively. With a mixture of large mass (1 kg) with similar shape the time taken to reach 280°C was 22 min. This period of time could be reduced perhaps, by spreading the mass into thin beds.

The period B is the period during which most reaction takes place. It was observed with the mixtures of 10g, 30g and 1 kg that the time taken was respectively 4, 8 and 18 min. As mentioned earlier this period of time is less dependent on the mass treated due to the intense reaction.

During periods C and D much of the remaining 10% of the mineral reacts. Normally 95% of the monazite had reacted by the end of period C. The last few percent of monazite were slow to react, as expected, and therefore the period D could be long compared with the earlier periods, depending on the required extent of reaction. It is thought that the small portion of the mineral which had been out of contact with the reagent up to the end of period C was reacting as sodium hydroxide slowly transported through the products.

### 4.2.3 Correlation on the reactivity

The characteristic features of the reaction between monazite and sodium hydroxide are that it is exothermic and it forms water vapour which is readily removed from the system. In any type of reaction the primary condition for reaction is to bring the reactants in contact with each other. When the contact is improved an increase in the reactivity is expected, particularly if the improved contact is maintained throughout the reaction. In a system of solid reactants if one of the reactants partly forms a liquid in one way or other, the contact between the two species would be much improved, leading to greater reactivity. As mentioned earlier, the heat produced by the reaction of monazite with sodium hydroxide could give rise to melting of small particles of sodium hydroxide in the vicinity of the reaction site (see Section 1.2, PART I). The effect will be promoted as the reaction proceeds and the temperature of the whole system approaches the melting point. A fast reaction can be expected once a small part of the system reacts, because it is probably self-sustaining.

The formation of a low melting mixture or compound would be one way of starting the reaction (e.g. the melting of a eutectic mixture of sodium hydroxide and sodium carbonate (22%) occurs at 284°C (23)).

On the other hand, in a number of experiments involving solid-solid reactions, Hedvall (24) has observed a maximum in the reactivity coinciding with a phase transition of one of the solids. In the reaction between monazite and solid sodium hydroxide the mineral is expected to be the solid having the dominant effect on the rate of reaction. As monazite itself does not undergo any physical or chemical transition below 1000°C no Hedvall effect was expected. On the other hand, sodium hydroxide undergoes two crystallographic phase changes in its solid state. If the assumption that rate is determined more by the mineral than by the sodium hydroxide is incorrect, any of the solid phase changes that sodium hydroxide undergoes between 25°C and 315°C could give rise to increased rate of reaction. Smothers, et. al.(25) have investigated in detail the phase changes of sodium hydroxide and came to the following conclusions:

Transition A: Melting of sodium hydroxide monohydrate at 65°C. The surface of the sodium hydroxide was distinctly fluid and the liquid phase disappeared at approximately 75°C and the surface was dry again.

Transition B: Evaporation of water from solution formed during transition A. Blisters in the sodium hydroxide were observed in the temperature range between 200 - 250°C.

Transition C: Transition of α-sodium hydroxide to β-sodium hydroxide (280 - 297°C).

Transition D: Melting of β-sodium hydroxide (315°C).

For the purpose of correlation, various results are arranged together in Fig. 21. As is apparent from the figure the reactivity of monazite is, to a considerable extent, associated with the physical changes occurring in the sodium hydroxide.

## Progress of reaction

The progress of reaction between monazite and sodium hydroxide as the mixture is heated can be explained as follows:

The monazite particles in the initial mixture are brought into close contact with sodium hydroxide as the monohydrate melts at 65°C. The initial reaction observed with the fine particles of monazite is believed to be due to the improved surface coverage of the mineral by the molten sodium hydroxide. The extent of reaction would be limited because (a) only a limited amount of $NaOH.H_2O$ is present, (b) once the surrounding sodium hydroxide is used up further transport of unreacted sodium hydroxide to the reaction site would be impossible if it is purely a solid-solid reaction. On further heating to ~270°C the mixture reacts rapidly due to the sum of the following effects:

(i) The crystallographic transformation of α-NaOH -> β-NaOH initiates the reaction.

(ii) The local liquifaction of more sodium hydroxide by the heat of reaction, and formation of a low melting eutectic with

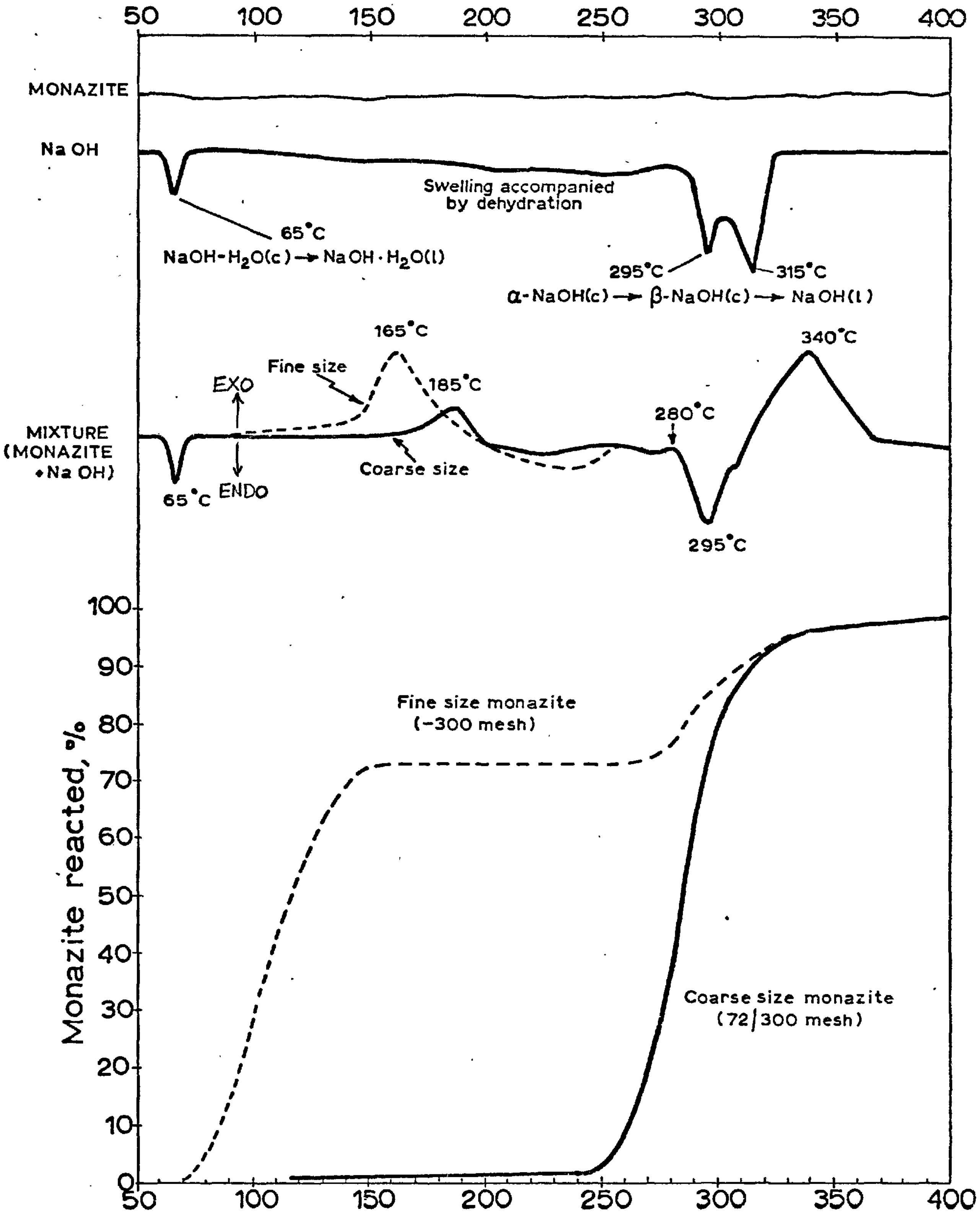


Fig. 21 Correlation of the reactivity of monazite with solid sodium hydroxide in terms of physical changes accompanied with sodium hydroxide.

other sodium compounds. During the course of heating, it was observed that the particles of monazite were coated with a thin film of molten sodium hydroxide while the thermocouple inserted into the mixed mass indicated 270°C.

(iii) Increased reactivity and mobility of liquid sodium hydroxide.

(iv) The ready removal of gaseous water formed, hence the equilibrium is never attained.

(v) The action of water vapour generated in stoichiometric quantities at the site of reaction which helps to break up and displace the solid product from the surface of unreacted mineral.

## 4.3 The physical nature of the products

The reaction products of monazite with solid sodium hydroxide were made up of highly porous aggregates of minute particles loosely bound together (See Figs. 22, 23 and 24). The various products were uniformly mixed together in the aggregate. Fig. 23 shows a portion of the aggregate or 'frit' and in Fig. 24 at higher magnification (X50). It is interesting to note two levels of aggregation. At low magnification the frit appeared to be an aggregate of particles of comparable size to the original monazite sand particles (see Fig. 23). At higher magnification each of these 'particles' is seen to be an aggregate of smaller particles of product. The net result is a frit containing wide channels through which a gas or liquid can flow readily to all of the 'particles', where further penetration can occur via shorter channels of smaller crosssectional area. This type of material is ideal for processing by gaseous or liquid reagents. The aggregates were readily disintegrated upon soaking in water. Fig. 25b shows the state of disintegration after 1 min. in cold water. The rare earth oxide residue left after disintegration in water was finely divided; the particle size was ~2μm (see Fig. 26).

× 8

Fig. 22 Some specimens of the reaction products (frits) from caustic fritting of

(A) Monazite (upper left)

(B) Wolframite (upper right)

(C) Columbite (lower left)

(D) Xenotime (lower right)

Fig. 23 Reaction product of monazite (frits) x 17. It shows a porous state of aggregation.

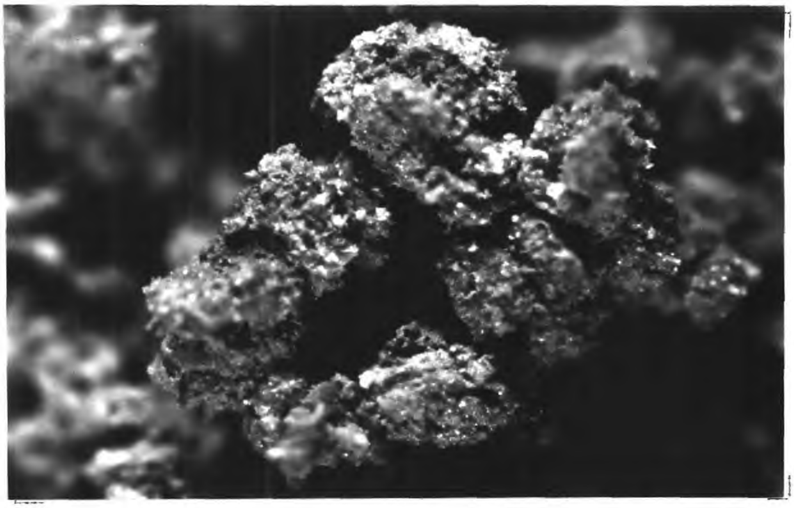
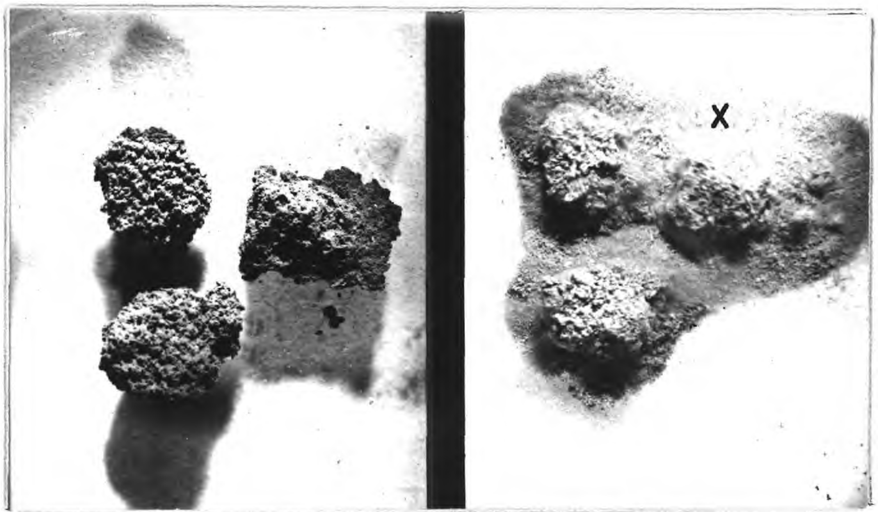


Fig. 24 Reaction product of monazite (frits) x 50. A magnified portion of the same frit as above. Each aggregate represents products from one monazite particle and consists of minute particles of products.



(a) (b)

Fig. 25 Monazite frits before (a) and 1 minute after (b) soaking in cold water, x 3.

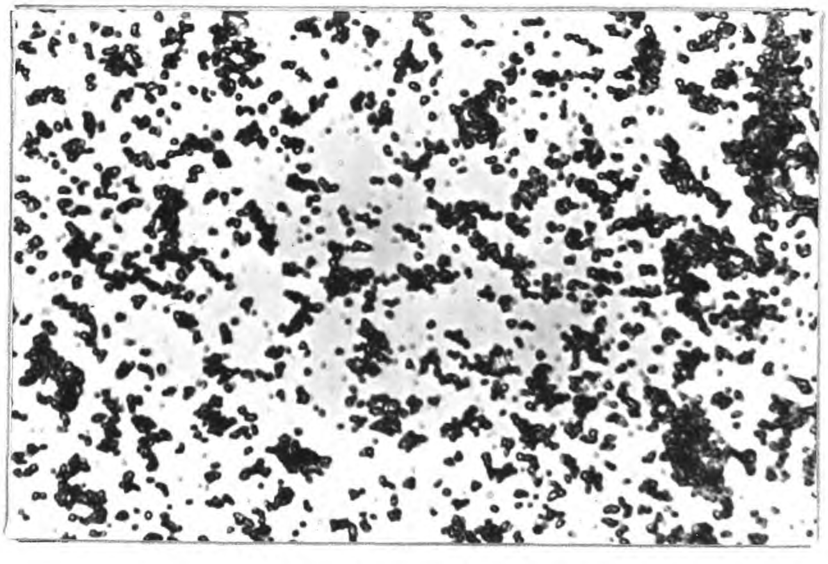


Fig. 26 Particles of rare earth oxides from monazite dispersed in water, x 625. A magnified portion of dispersed phase in Fig. 25 (b) marked 'x'. Particle size: 1-2μm.

## 4.4 Subsequent processing

The residues after water leaching of the monazite frits contain all the rare earths and thorium as oxides. The subsequent processing would require dissolution of the oxides in acids followed by purification and separation of the values. The present work is concerned only with the dissolution of the oxides.

In earlier reports it has been pointed out that the reaction conditions during the caustic soda treatment influence the rate of dissolution of the oxides. After caustic solution treatment Bearse et. al.(3) found that the thorium was converted into a refractory material at the higher temperatures (200°C) which was difficult to dissolve in mineral acids. Kaplan and Uspenskaya (10) mentioned that difficulties were encountered in dissolution of thorium and rare earth oxides formed by alkali fusion at 400 - 500°C.

The first object of the dissolution experiments was, therefore, to establish whether or not the oxides formed by fritting process were equally refractory as these produced by the fusion method. It was found that the oxides formed by the fritting process were readily dissolved in common mineral acids. In the following sections the rate of dissolution and optimum conditions for dissolution are described.

### 4.4.1 The influences of temperature and concentration on the dissolution of oxides in HCl

The leaching curves for the washed oxides formed at 360°C are shown in Fig. 27. The result showed that the oxides dissolved completely in undiluted concentrated hydrochloric acid at 60°C within an hour. Three elements; lanthanum, neodymium and thorium dissolved completely within 20 minutes but cerium reached its limiting dissolution only after one hour of leaching.

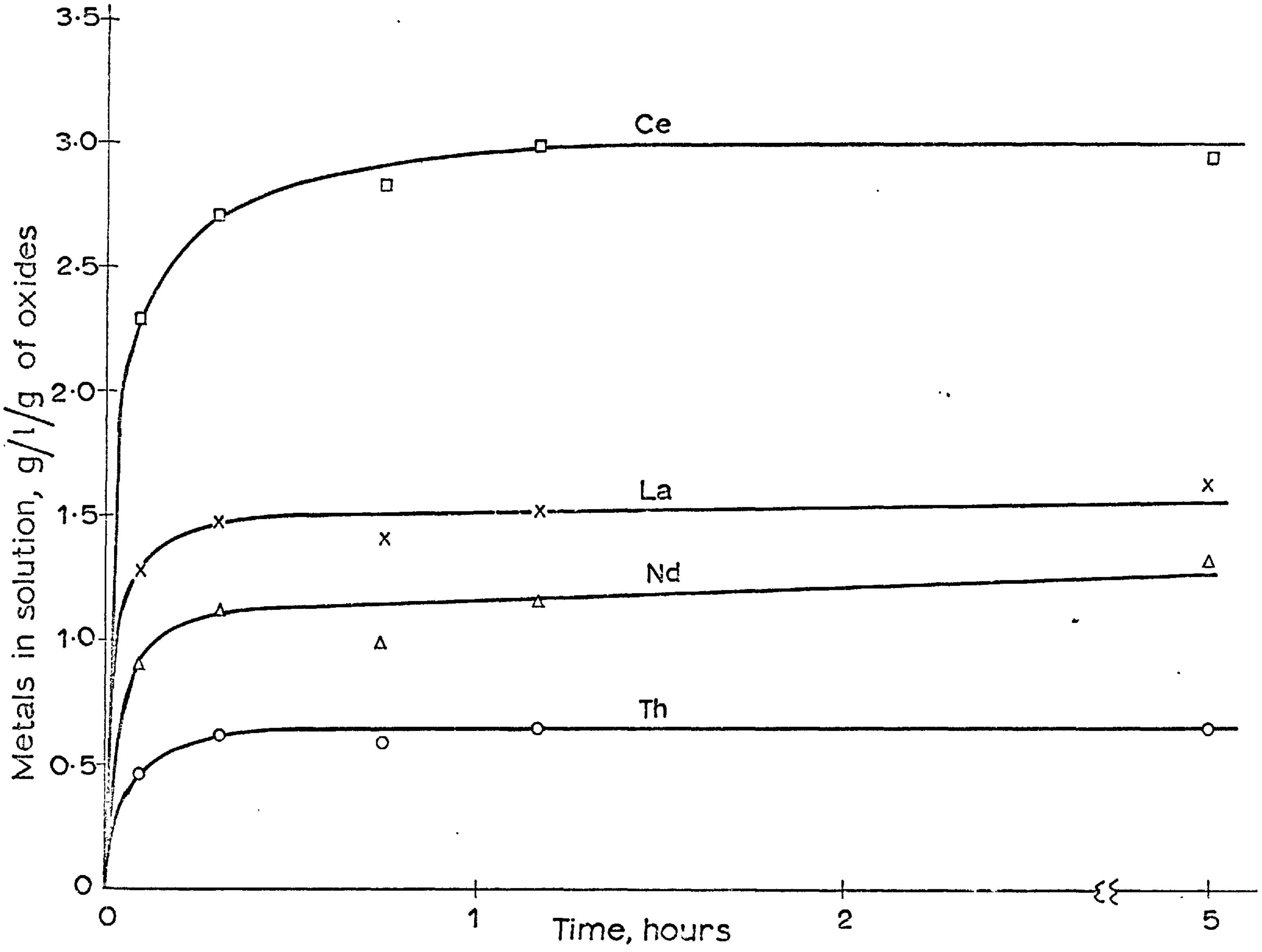


Fig. 27 Leaching curves for precipitated oxides from monazite by undiluted H Cl (11.4 N) at 60 ± 1°C.

Similar tests were carried out at lower temperatures. The results obtained were similar to those obtained at 60°C (see Figs. 28 and 29). All the elements except cerium were almost completely dissolved within half an hour at 40°C. (Fig. 29). Again, the rate of dissolution was less with cerium, but complete dissolution was obtained within one and half hours at the low temperature.

### 4.4.2 The rate of dissolution in other acids

The influence of the different mineral acids on the dissolution at various temperatures and concentrations was tested and is summarized in Table 10. It can be seen that hydrochloric acid is the most effective and nitric acid is the least effective under comparable conditions. It was observed that sulphuric acid of the concentrations used, produced acid insoluble but water soluble white precipitates. Optimum conditions for complete dissolution were respectively with conc. HCl (11.5N) at 60°C (within 1 hour), 23N $H_2SO_4$ at 60°C (within 1 hour) and conc. $HNO_3$ at 110°C (within 2 hours).

### 4.4.3 The influence of the heating time in the fritting reaction

The effect of various lengths of heating time at 360°C on the dissolution of oxides was investigated. The results showed that there was no difference in the extent of acid dissolution. All the oxides formed during various lengths of time dissolved completely and in a similar manner leaving only a small quantity of gelatinous precipitates (1.7%) which were later confirmed to be siliceous matter.

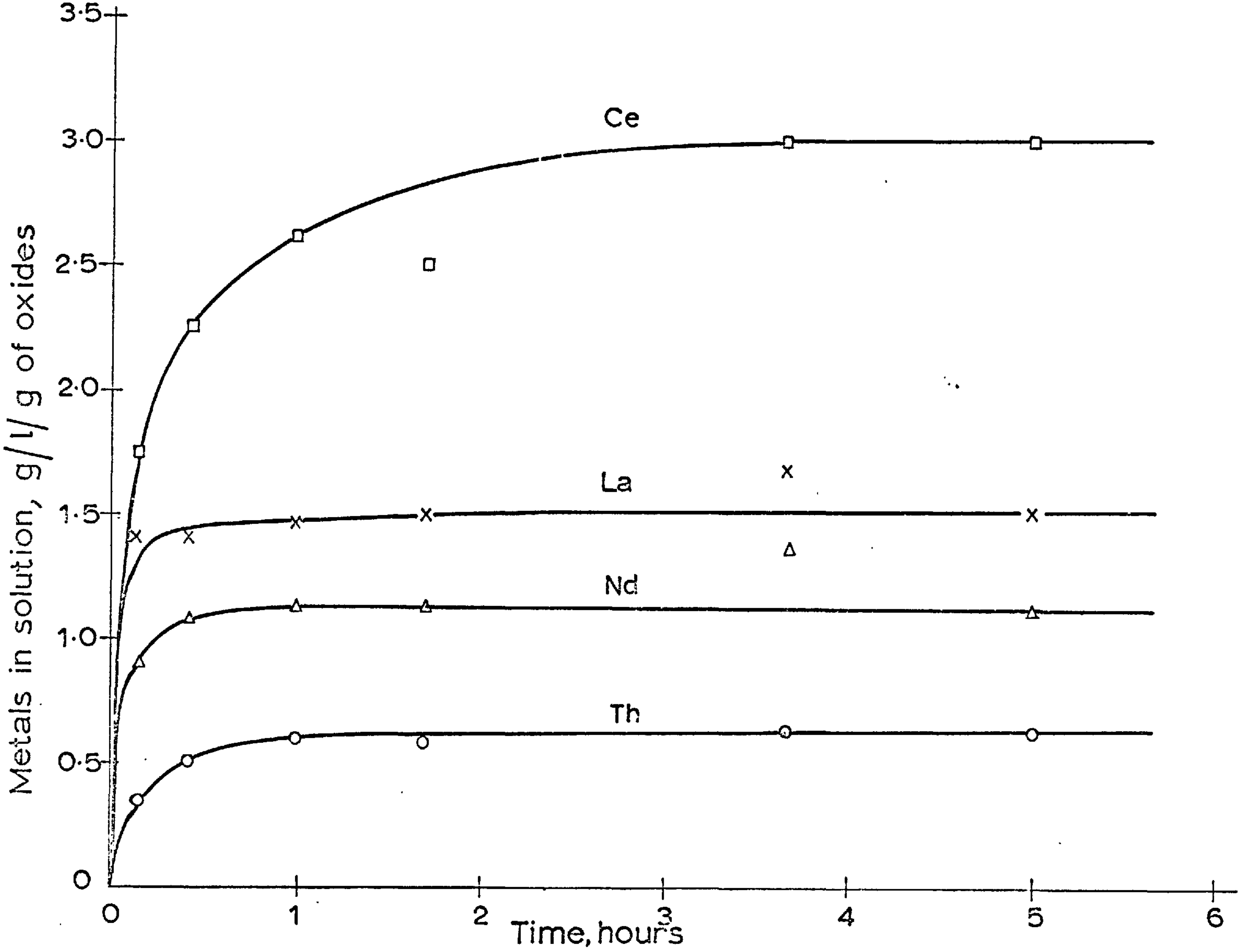


Fig. 28 Leaching curves for precipitated oxides from monazite by undiluted HCl (11.4N) at 50±1°C.

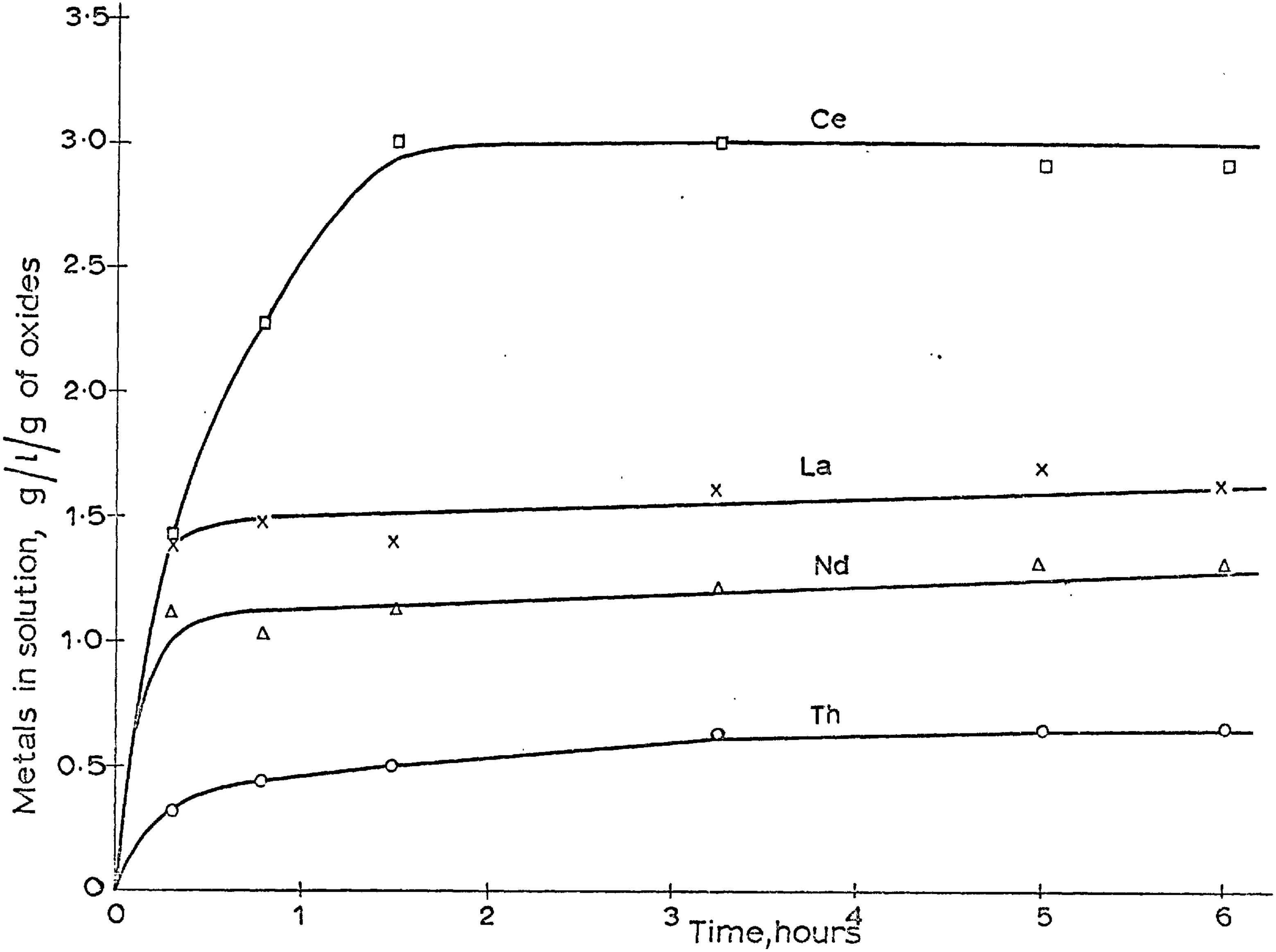


Fig. 29 Leaching curves for precipitated oxides from monazite by undiluted HCl (11·4 N) at 39±1°C.

Table 10. Dissolution in acids of Th and rare earth oxides from monazite at various concentrations of acid temperatures.

| Acid and Conc. | | 110°C | 60°C | 50°C | 40°C |
|---|---|---|---|---|---|
| HCl | 11.5N (undiluted) | — | Complete within 1 hr. | Complete within 1 hr. | Complete within 1.5 hrs. |
| | 9 N | — | Complete within 7 hrs. | — | — |
| | 6. N | — | Incomplete within 24 hrs. | — | — |
| $H_2SO_4$ | 23 N | — | Complete within 1 hr | — | — |
| | 11.5 N | — | Complete within 4.5 hrs. | — | — |
| $HNO_3$ | 15.8 N (undiluted) | Complete within 1 hr. | Incomplete within 24 hrs | — | — |
| | 11.5 N | — | Incomplete within 24 hrs | — | — |

### 4.4.4 Influence of the quantity of acid

Acid dissolution tests with the washed oxides were carried out using various proportions of hydrochloric acid to rare earth oxides. The samples were taken in a 250ml conical flask with a funnel placed on its top and heated on a constant temperature hot plate. The temperature of the acid solution reached 60$^{\circ}$C within 5 minutes and was maintained at $65^{\circ} \pm 5^{\circ}$C during reaction. The clarity of the suspension was noted every 5 minutes. The results are shown in Table 11, which indicates the time at which clear solution was first observed. The optimum quantity of hydrochloric acid to dissolve the oxides completely within half an hour was found to be 5ml/g oxides. The ratio can be reduced to 3ml/g oxides, but longer time will be required (1hr 40min). With a ratio of 2ml/g (approximately stoichiometric quantity) the dissolution was still incomplete even after 2 hours.

Table 11. Time required for complete dissolution of oxides at various ratio of HCl, ml/g solids. (Solution temperature: $65 \pm 5^{\circ}$C)

| Time, min.<br>Ratio | 5 | 10 | 15 | 20 | 25 | 30 | - | 100 | - | 120 |
|---|---|---|---|---|---|---|---|---|---|---|
| 60ml/g oxides | X | X | O | | | | | | | |
| 30 " " | X | X | O | | | | | | | |
| 20 " " | X | X | X | O | | | | | | |
| 15 " " | X | X | X | O | | | | | | |
| 10 " " | X | X | X | O | | | | | | |
| 7.5 " " | X | X | X | O | | | | | | |
| 5 " " | X | X | X | X | X | O | | | | |
| 3 " " | X | X | X | X | X | X | | O | | |
| 2 " " | X | X | X | X | X | X | | X | | X |
| | | | | | | | | (incomplete) | | |

Notes: X for incomplete dissolution,
O for complete dissolution.

## 5. Tests of the fritting method on commercial monazite concentrates

This section consists of two parts: in the first part, small scale tests on various monazite samples; and in the second part, a large scale test with 0.5kg commercial concentrates will be described. The primary object of these experiments was to test the applicability of the process to a wide variety of commercial concentrates and on a larger quantity than in the early tests. The results were compared with the original monazite (Korean Monazite Sample A) in terms of fritting and dissolution of the water-leached oxides in acids. No major differences from the previous results were observed in either series of tests.

### 5.1 Small scale tests on various monazite samples

### 5.1.1 Decomposition

Tests of fritting were carried out using the previously described, optimum conditions for monazite samples from 8 different localities (See Table 12). As much as 15g of each commercial concentrate, as received (unground), was mixed with an equal amount of sodium hydroxide powder and heated to 360°C for 1 hour. All the frits produced from the various samples showed similar physical properties, i.e. porous nature, ready water leaching, etc. The colour of the frits varied slightly from light brown to brown due to the impurities. Decomposition was almost complete in all cases leaving only refractory impurity minerals such as ilmenite, cassiterite, chromite, zircon, garnet, etc. unattacked. The quantity of residual sands (impurity) varied from one sample to another (see Table 12).

### 5.1.2. Acid-leaching of the precipitated oxides.

During the water leaching stage the oxides, as a fine suspension, were separated from the unreacted sands by decantation and dried at 110°C. A sample from each specimen of dried oxide was placed in a beaker covered with a watch glass and dissolved in concentrated hydrochloric acid (constant solid : acid) by heating on a constant temperature hot plate. The rate of dissolution varied from one sample to another but all the samples gave complete dissolution within 30 minutes, which is comparable to that obtained with the oxides from the Korean Monazite sample A.

Table 12. Results of tests on various commercial monazite sands

| Sample | Unreacted sands(%)* | Oxides produced(%)* | Dissolution time in in conc. HCl(30ml/g) at 70°± 5°C |
|---|---|---|---|
| Australian | 19.9 | 64.2 | 25 min |
| Ceylonese | 7.4 | 73.5 | 15 " |
| Congolese | 14.7 | 63.3 | 30 " |
| Indonesian | 17.2 | 64.6 | 15 " |
| Korean(B) | 18.5 | 62.3 | 15 " |
| Korean(C)** | 9.0 | 69.3 | 20 " |
| Malayan | 26.7 | 58.5 | 15 " |
| Nigerian | 13.1 | 75.8 | 25 " |
| Venetian | 8.7 | 67.3 | 30 " |
| Korean(A) (Original sample) | 5.9 | 73.1 | 20 " |

* The percentage is referred to monazite sands.
** Same sample as scale-up test or the 1kg test.

## 5.2 Large scale tests on commercial monazite concentrate

A batch test was carried out using 0.5kg of commercial unground monazite concentrate (Korean monazite sample C). The conditions of treatment were essentially similar to that of the small scale tests except that the muffle furnace was initially at a slightly higher temperature (10°C) to offset the cooling effect caused by introducing a cold charge.

### 5.2.1 Procedure

#### (i) Heat treatment and water leaching

The mixture 0.5kg of commercial monazite concentrate and 0.5kg of ground sodium hydroxide was placed in two rectangular boxes made of plain iron sheet (10cm x 15cm x 5cm) and heated in a preheated electric muffle furnace (370°C) for an hour. The frits were leached with water in a 4 litre beaker by manual stirring. The pulp was allowed to settle and the supernatant solution was siphoned out. This operation was repeated twice more with fresh hot water and then with warm 1% sodium hydroxide solution. Unreacted sands were separated by repeated suspension and decantation. The total quantity of water consumed was 10 litres. The solution was assayed for phosphorus and rare earth metals. The final oxide slurry was centrifuged and dried in an oven at 110°C.

#### (ii) Acid dissolution

Three 5g samples were taken from the dry oxides and dissolved in conc. hydrochloric acid at 60°C using acid to oxides ratio of 5ml/g oxides. During heating on a hot plate, the beakers covered with watch glasses, were occasionally shaken.

### 5.2.2 Results

The product of heat-treatment was the usual light brown porous frit; it was uniform throughout and just as readily leached as those obtained from the small scale tests. As shown by the heating curves (Fig. 30) the exothermic effect which was generally observed in small scale tests, again appeared when the temperature of the sample reached ~270°C. The maximum temperature obtained was a few degrees higher than the pre-set furnace temperature.

The products of reaction after heat-treatment weighed as much as 953g. After water leaching of the whole frit 363g of oxides and 41g of unreacted sands were obtained. The extent of decomposition in terms of the phosphorus content was 95% which could probably improved by further test work.

The washed oxides of rare earths and thorium dissolved completely in conc. HCl at 60 ± 5°C. A clear solution, orange yellow colour, was obtained in 20 min. leaving behind a small quantity of white siliceous suspension (2.4% of the washed oxides) which was easily removed by filtering. Thus, no difficulties were encountered with processing the frits in this larger scale which were comparable to those reported for the products of fusion.

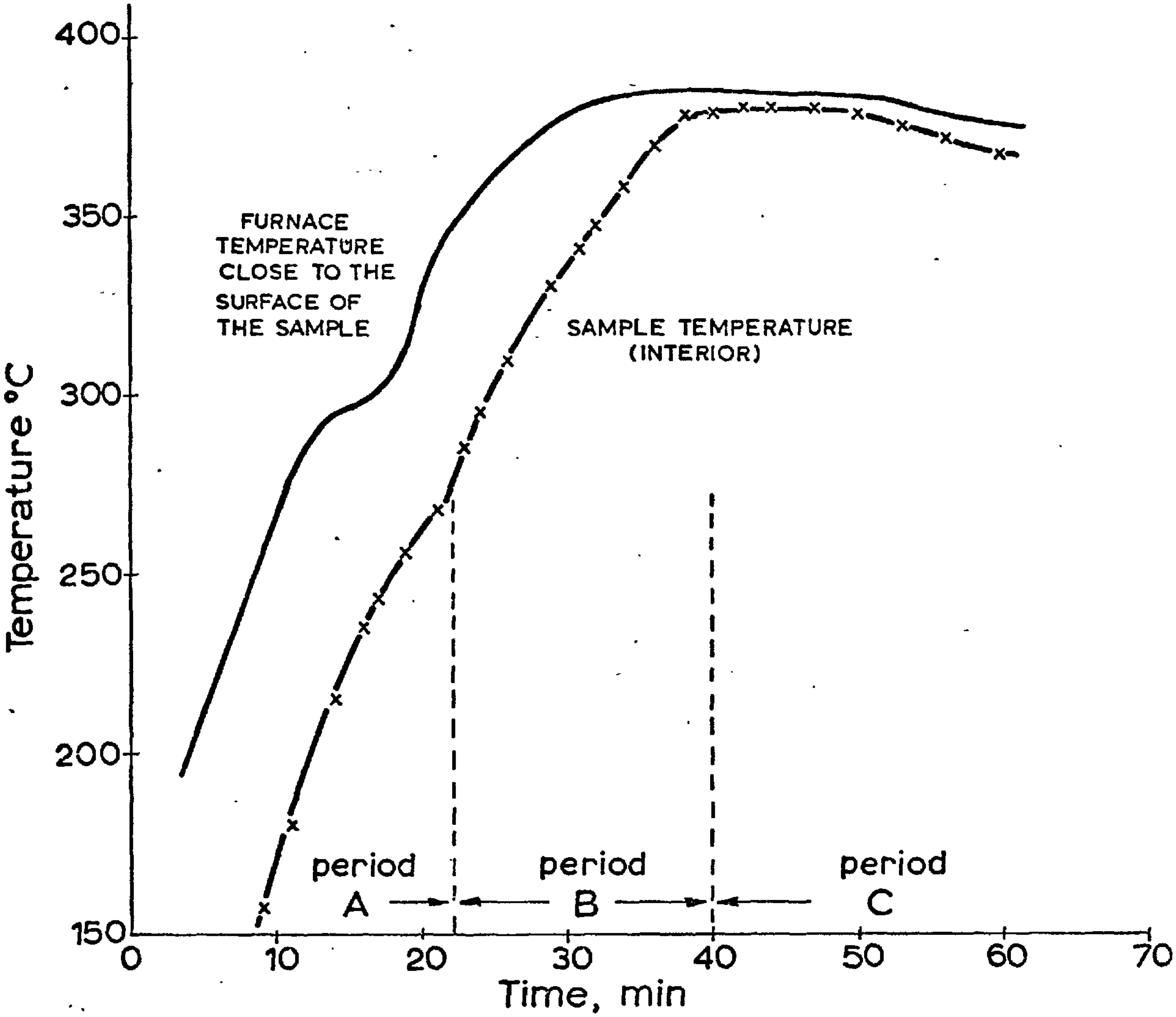


Fig. 30 Heating curves for the sample mixture (1 Kg.). Chromel-alumel thermocouple was inserted in the centre portion of the mix.

# PART III

# APPLICATION TO OTHER MINERALS

## 1. Introduction

This part of the thesis is concerned with the application of the fritting process to other high value economic mineral concentrates containing a single mineral; e.g. wolframite and columbite. The application to physically unseparated pairs of minerals such as wolframite-cassiterite mixed concentrate will be described under the heading: Selective Reaction (Section 5, PART III).

The preliminary reactivity tests by D.T.A. indicated that these minerals react with sodium hydroxide at moderate temperatures and as the products are expected to be similar chemically (see equation in Table 3), the study was extended to include these minerals. The object of this part of the study is twofold; first to understand more about the process, particularly whether the same critical temperatures occurred and second to obtain the optimum processing conditions. Hence, the investigation of the detailed nature of the tungstate and niobate products, for instance, was neglected.

The influence of temperature, time and ratio of sodium hydroxide have been determined. The physical changes taking place in the mixture during the course of heating particularly the liquifaction effect at lower temperatures than the melting point of sodium hydroxide were also observed. The following chapters describe the findings on the individual minerals.

## 2. Wolframite

### 2.1. Materials and Methods

Wolframite is a solid solution of iron and manganese tungstates generally represented by the chemical formula $(Fe,Mn)WO_4$. A high grade wolframite concentrate, of unknown origin, was purified by magnetic seperation and vanning the closely sized fractions. A polished section of the 72/200 mesh fraction was examined by a reflected polarized light microscope and by an electron-probe microanalyser. This examination showed that the level of the tungsten content was uniform over a number of grains, but the iron and manganese contents varied from one grain to another but not within a grain. For example, the number of counts from 4 grains randomly selected indicated manganese contents between 8 and 18%, and iron contents between 16 and 4%, whereas the tungsten content remained constant at 53%. From the examination of the same polished section under reflected polarized light it was noted that some grains of huebnerite were present. In other words the sample was mineralogically a mixture of the two end members and intermediates.

The result of chemical assay of the purified wolframite showed 53.6%W, 5.3%Fe, 6.95% Mn and 0.3%Ca. The Same purified 72/200 mesh fraction was used for the reaction tests.

### Methods

The preparation of the reactants mixture and the heat-treatment were conducted in a similar way as that described for monazite (3.1, PART II). The reaction products were leached with water and the centrifuged supernatant solution containing sodium tungstate was analysed for tungsten by atomic absorption spectrophotometry using a Hilger and Watts' Atomspec H1170 (tungsten hollow cathode lamp for the light source, wavelength at 4009Å using oxidising flame with nitrous oxide - acetylene gas mixture.)

The extent of reaction was determined from the quantity of tungsten which was rendered soluble.

## 2.2 Experimental Results

### 2.2.1 Effect of the temperature

The reactivity of wolframite with sodium hydroxide is shown in Fig. 31 as a function of temperature. A small increase in extent of reaction (in a fixed time of 40 min.) was observed at 200°C but on further heating to around 250°C there was a marked increase. Most of the mineral reacted around 300°C and complete reaction was obtained in 40 min. by heating to 340°C. The products of reaction at this last temperature were of the same porous and friable nature as those obtained with monazite but the colour was greenish blue (See colour photograph Fig.22B) suggesting the formation of sodium manganate. It was notable that the products formed at 400°C were partly in the fused state and those heated to 450°C were a totally fused mass.

### 2.2.2 Effect of the ratio of sodium hydroxide

The reaction of wolframite at various weight ratios of sodium hydroxide to mineral was investigated by heating the mixtures to 350°C for 40 minutes. The results are shown in Fig. 32, from which it can be seen that the optimum weight ratio for satisfactory decomposition is 1.20.

### 2.2.3 Influence of the heating period

The time dependence of the decomposition was investigated by placing the mixture in a furnace preheated to 350°C for various lengths of time. The ratio of sodium hydroxide to wolframite used for the tests was 1.20. During the course of heating, the change in physical appearance of the reactant mass was also examined by the naked eye in order to obtain some apparent evidence for the local liquifaction effect discussed

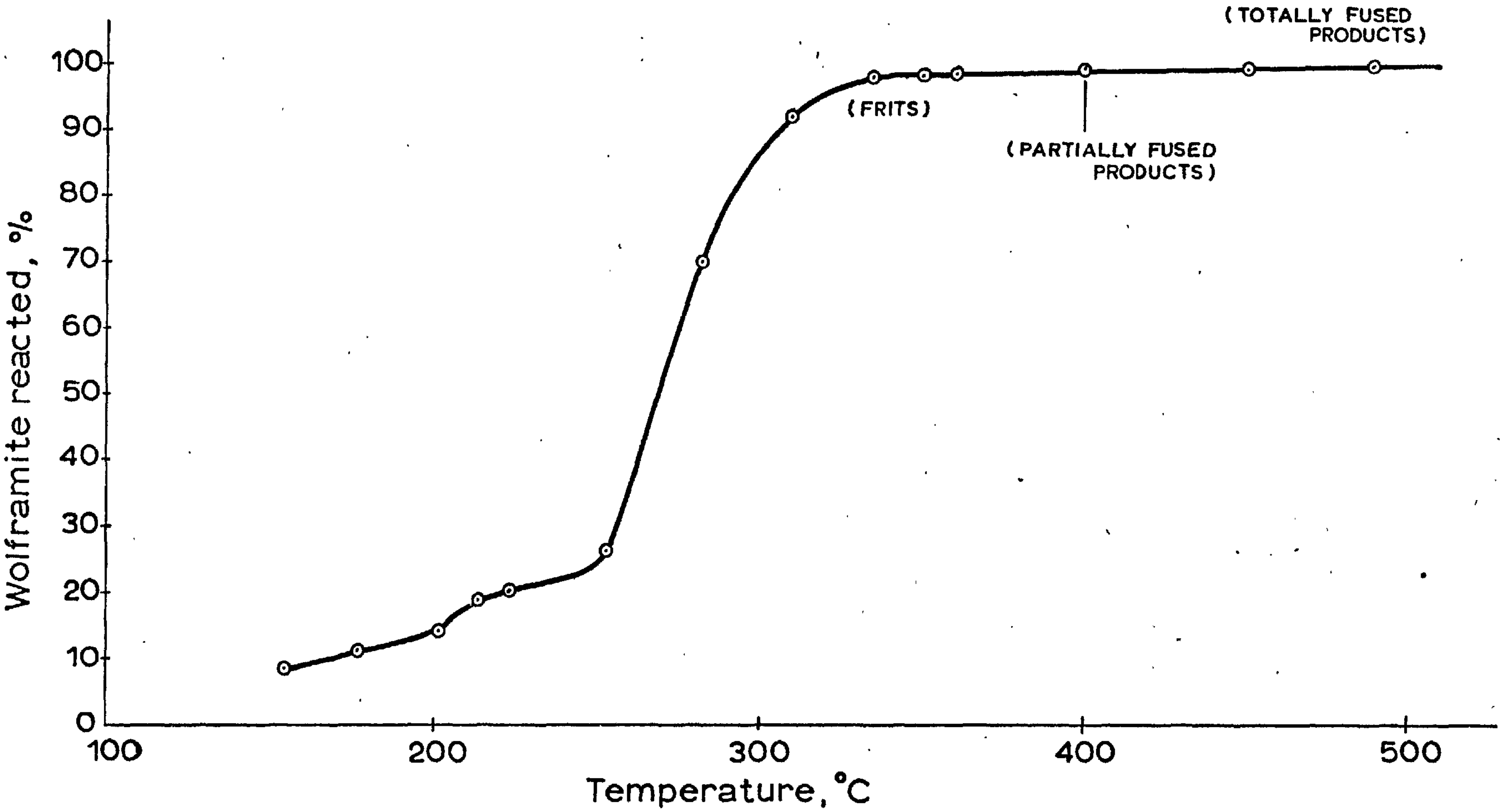


Fig. 31 Reaction of wolframite with sodium hydroxide as a function of temperature. ( Size of mineral : 72/200 mesh, Na OH/mineral = 1·2, heating for 40 mins.)

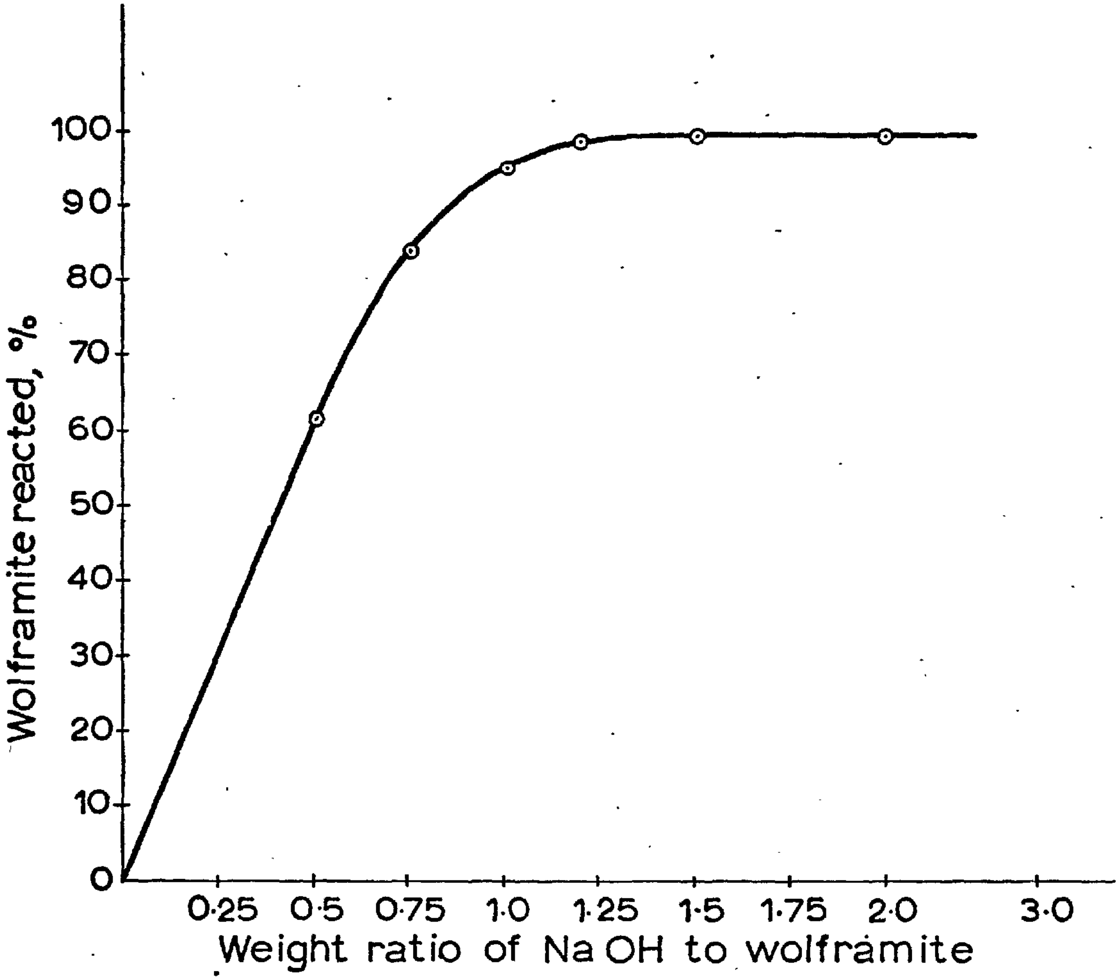


Fig. 32 Reaction of wolframite as a function of weight ratio of sodium hydroxide to mineral.
(Size of mineral : 72/200, heated to 350°C for 40 mins.)

previously. The observation was as follows (Table 13):

Table 13. Experimental observations of the physical change of the wolframite - NaOH solid mixture during heating.

| (Time) | (Temperature of the sample mix) | (Description of Observation) |
|---|---|---|
| 6min | 275°C | Initiation of reaction (indicated by partial change in colour to brown, local melting of NaOH and evolution of gas). Endotherm in heating curve. |
| 8min | 300°C | Continuation of reaction indicated by local fusion and evolution of gas phase. Colour of the solid mix turned from black to brown throughout the mass. |
| 15min | 355°C | Continuation of reaction. The rate of gas evolution slowed down. The colour was brown. |
| 30min | 350°C | The temperature reached the preset value. Gas evolution was not distinct. The surface of the mass showed dry appearance. |
| 40min | 350°C | No change except that the colour changed from brown to deep blue-green; suggesting formation of $Na_2MnO_4$ in later stage of reaction. |
| 60min | 350°C | Same as above.<br>No further change apparent. |

From the above observation it was again evident that the local liquifaction of the reagent takes place even when the temperature of the whole system is below the melting point of sodium hydroxide.

The extent of reaction for various periods of heating are shown in Fig. 33. As can be seen from the figure, most of the mineral particles had reacted (94%) during the first 20 min. of heating, but it required a further 40 min. to complete the remaining few percent. In other words a heating period of 1 hour was adequate for complete reaction.

As was noted in Table 13, the products of wolframite obtained after shorter periods than 30 min. were brown in colour and no green colour in the solution was observed after leaching indicating that sodium manganate was formed only in the later stages of heating in the presence of excess sodium hydroxide.

## 2.3 Summary of the results from wolframite

The experimental results on wolframite showed that the mineral can be processed with solid sodium hydroxide by heating the mixture in weight ratio of NaOH/mineral = 1.2 to 350°C for 1 hour. Fine-grinding of the mineral is unnecessary and the resultant reaction products can be obtained in a form similar to those obtained with monazite. The temperature at which the reaction had started within 20 min. was also similar to that for monazite. Heating to above 400°C left the products in a fused state. Thus, the optimum temperature range for the fritting process for wolframite is between 340 and 390°C. During the course of heating a thin liquid film coating the mineral particles (indicated by the shiny appearance)was observed when the overall temperature of the reactant mixture was 270°C. The physical form of the mixture remained unchanged at this time (on total fusion the reactant mixture normally sank to the bottom changing its shape). Also, evolution of a gaseous product (steam) was noted at around 275°C indicating the intense reaction. Similar phenomena were observed with monazite but were less apparent to the naked eye (probably due to the colour of the original mineral). These, together with

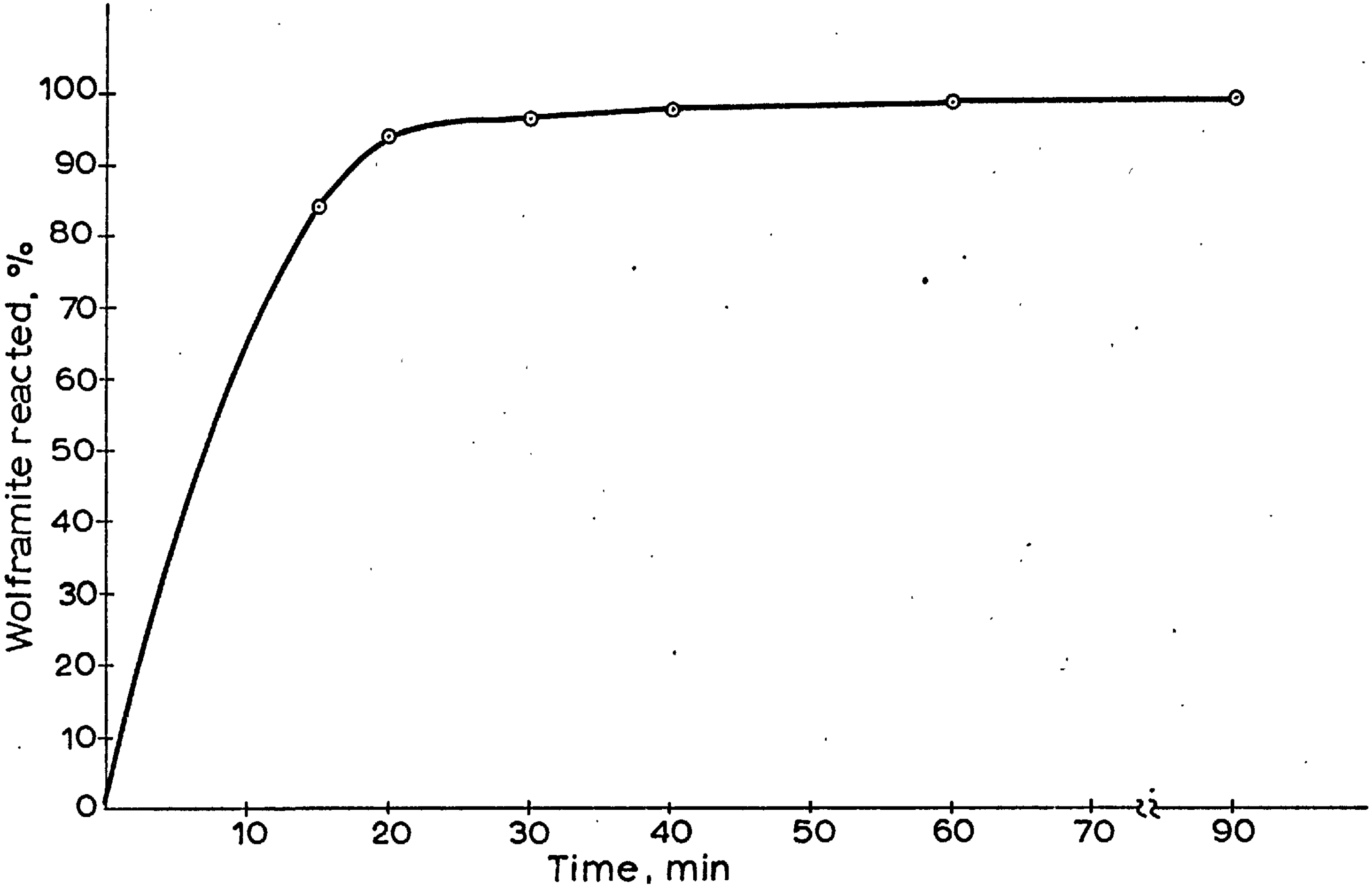


Fig. 33 Reaction of wolframite with sodium hydroxide as a function of residence time in the furnace preheated to 350°C. (Size of mineral: 72/200 mesh, Na OH/mineral = 1·2)

information on the extent of reaction, substantiate the postulate (section 4.2.3) that the high reactivity around 280°C is due to the resultant effects of exothermic reaction leading to local liquifaction and improved transport of the reagent and also the Hedvall effect.

The chemical interaction of wolframite with sodium hydroxide in the presence of oxygen may be described as follows:

$$2FeWO_4 + 4NaOH + \tfrac{1}{2}O_2 = 2Na_2WO_4 + Fe_2O_3 + 2H_2O$$

In the presence of excess sodium hydroxide, sodium ferrite may be formed:

$$Fe_2O_3 + 2NaOH = 2NaFeO_2 + H_2O$$

However, the reaction will be reversed on water leaching to give hydrated ferric oxide. The reaction of the manganese part of wolframite may be written as

$$MnWO_4 + 2NaOH + \tfrac{1}{2}O_2 = Na_2WO_4 + MnO_2 + H_2O$$

The manganese dioxide formed will be converted to form sodium manganate on further oxidation and in the presence of excess sodium hydroxide:

$$MnO_2 + 2NaOH + \tfrac{1}{2}O_2 = Na_2MnO_4 + H_2O.$$

## 3. Columbite

### 3.1 Materials and methods

A high grade commercial concentrate of columbite originally from Nigeria was obtained through Mr T. Deans, Institute of Geological Sciences, London. W.C.1. The size distribution and chemical assay of the concentrate are shown respectively in Tables 14 and 15. A polished section of the sample was examined by electron probe micro-analyser and showed that the concentrate consisted of mainly columbite but with some tantalite as separate grains. The level of the niobium content varied even within a grain. The contents of iron and manganese were approximately constant but those of niobium and tantalum varied.

The sample was used for the reactivity tests after removing minor quantities of light and highly magnetic impurity minerals. Preparation of the sample mixture and the heat-treatment were conducted similarly to the monazite tests. A simplified method of determining the percentage of reaction was employed. The heated mass was leached first by water, and the reacted and soluble portion of the mineral was removed by decantation. The coatings adhering to the unreacted mineral were dissolved by hydrochloric acid in the presence of a small quantity of sodium fluoride. The dry weight of the remaining solid was used for calculating the unreacted portion of the mineral. This method was checked by chemical determination and gave approximately 2% greater values for the percentage of reaction.

### 3.2 Results on Columbite

#### 3.2.1 Effect of the temperature

The influence of temperature on the reactivity of columbite with sodium hydroxide was investigated for two size fractions: 72/200 mesh (standard size fraction for all the minerals in this

Table 14. Screen Analysis of the Nigerian Columbite Concentrate.

| mesh, B.S. | wt.% | Cummulative wt. % |
|---|---|---|
| +36 | 5.2 | 5.2 |
| 36/52 | 20.2 | 25.4 |
| 52/72 | 37.7 | 63.1 |
| 72/100 | 25.5 | 88.6 |
| 100/150 | 10.3 | 98.9 |
| 150/200 | 1.0 | 99.9 |
| -200 | 0.1 | |
| Total | 100.0 | |

Table 15. Chemical Analysis of the Nigerian Columbite

| Elements | wt. % |
|---|---|
| $Nb_2O_5$ | 66.2 |
| $Ta_2O_5$ | 7.0 |
| $TiO_2$ | 1.9 |
| FeO | 18.0 |
| MnO | 2.0 |
| $SnO_2$ | 2.7 |
| Total | 97.8 |

work for comparative purposes) and 52/100 mesh fraction (mean size of the particular commercial concentrate). All the tests were carried out using the same weight ratio (NaOH/mineral = 1.2) and heating for 1 hour. The results are shown in Fig. 34. Practically complete reaction was achieved at 520°C for the 72/200 mesh fraction. The temperature required for the unground commercial columbite was 20°C. higher. There was no dectectable reaction at either the solid phase transition temperature or on melting of sodium hydroxide, although fine sizes (-300 mesh) of the mineral showed reactivity at a temperature as low as 180°C (detected by D.T.A.). On further heating above the melting point of sodium hydroxide it was observed during the experiment that the rate of evolution of gas increased, i.e. the rate of reaction was accordingly greater. The products of an incomplete reaction at 415°C. revealed that the mineral grains were covered with a hard product layer which adhered firmly and was only removed by crushing or hard rubbing. Chemically it was a sodium niobate-tantalate mixture, which dissolved partially in hydrochloric acid but completely in the presence of fluoride or hydrofluoric acid.

All the products which were obtained by heating to a temperature higher than 450°C were in the form of loose aggregates (see colour photograph Fig. 22C). Also it was observed that most of the incomplete reaction products gave a fused mass.

### 3.2.2 Effect of the ratio of sodium hydroxide

In order to test the effect of the ratio of sodium hydroxide on the reaction of columbite, mixtures of various weight ratios of sodium hydroxide to mineral were heated to 550°C for an hour. The results of the tests are shown in Fig. 35, from which it is seen that most of the mineral (>95%) reacted at the weight ratio of 1.0, however 1.2 was required for complete reaction. Weight ratios greater than 1.2 were

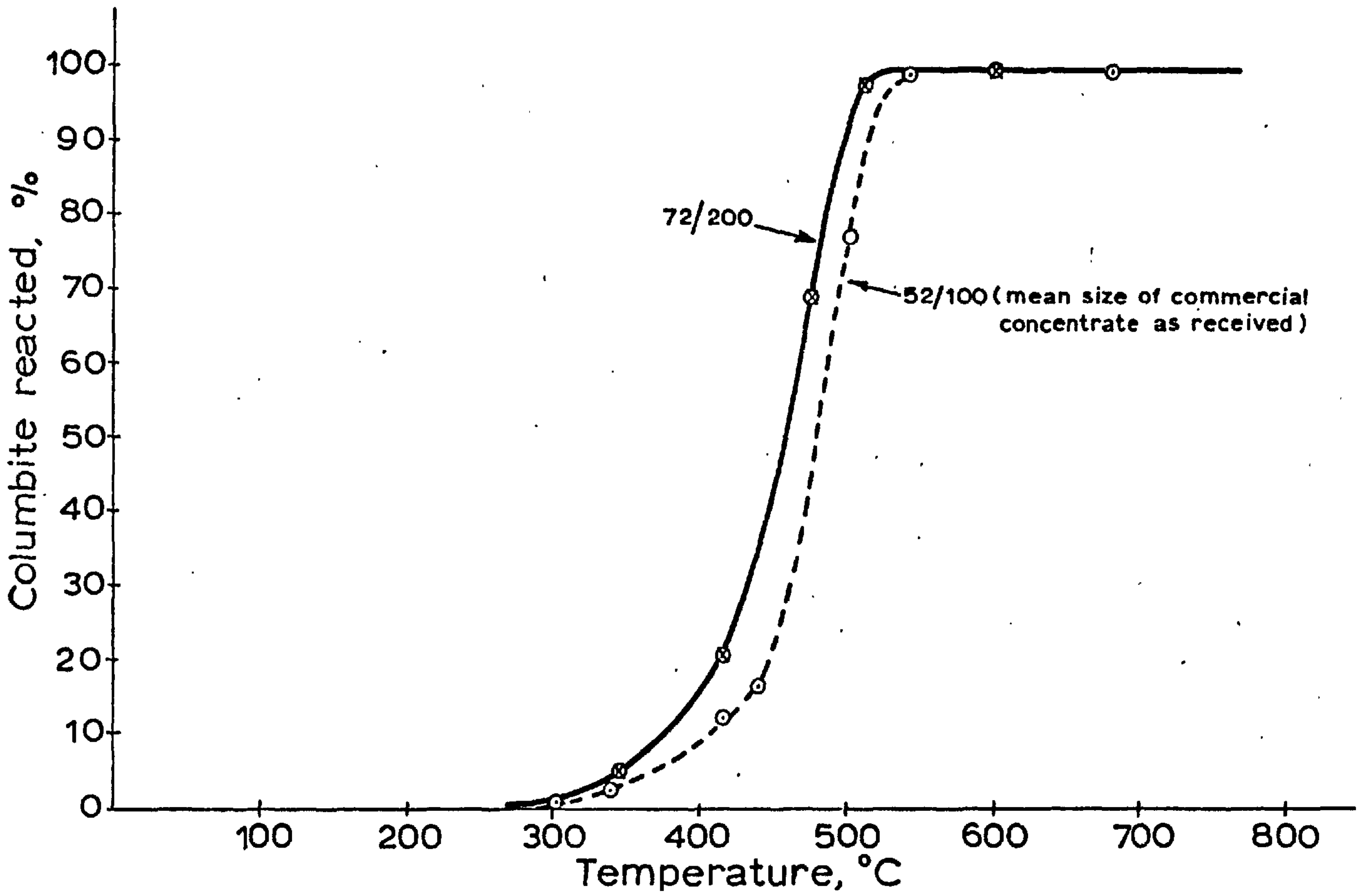


Fig. 34 Reaction of columbite with sodium hydroxide as a function of temperature for two size fractions (72/200 and 52/100 mesh). (NaOH/mineral = 1·2, heated for 1 hour)

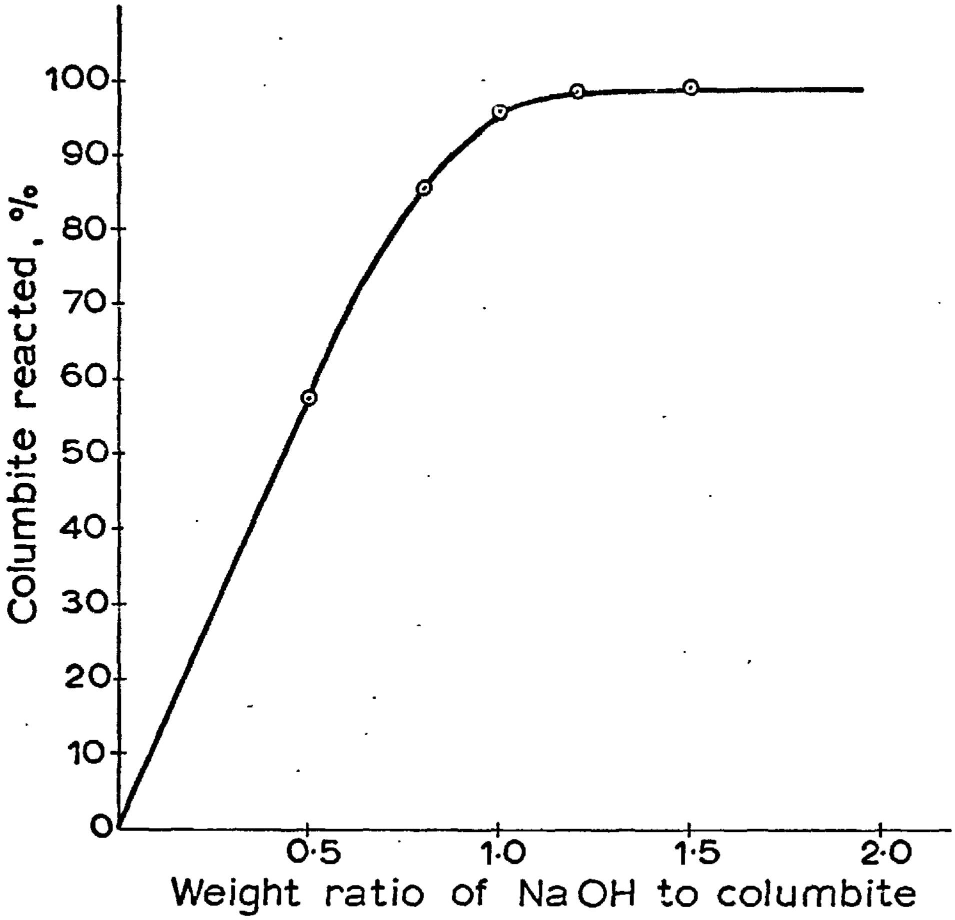


Fig. 35 Reaction of columbite as a function of weight ratio of NaOH to mineral. (Size of mineral: 52/100 mesh heated to 550°C for 1 hour)

unnecessary and rather harmful, as the products from excess sodium hydroxide were in the form of a fused hard mass which was difficult to leach.

### 3.2.3 Effect of time of heating

The effect of time on the reaction of columbite was investigated at 550°C using a fixed weight ratio of sodium hydroxide to mineral of 1.20. The results are shown in Fig. 36. Almost complete reaction (94%) was achieved within a short period of time (20min.) but an additional 40 minutes of heating were required to react the remaining few percent. In other words the optimum time of heating for complete reaction of commercial columbite sands was 1 hour at 550°C with the weight ratio of sodium hydroxide to mineral at 1.2.

## 3.3 Summary of the results from columbite

The experimental results have shown that the processing of columbite by caustic fritting is possible. The quantity of sodium hydroxide required can be reduced to less than half that required by the conventional fusion method; also the fine grinding to pass 300 mesh required by the current industrial process(4)(26) is unnecessary. The usual concentrate commercially available (52/100 mesh) can be directly treated without further grinding. The product of heating is not a fused mass which the conventional fusion process produces, but it is in a suitable form for the subsequent leaching.

The optimum processing conditions obtained with the Nigerian unground concentrate were to heat the mixture in weight ratio of NaOH/mineral = 1.2 to 550°C for 1 hour.
The chemical reactions occurring between columbite and sodium hydroxide may be written for iron niobate and tantalate (R:Nb,Ta);

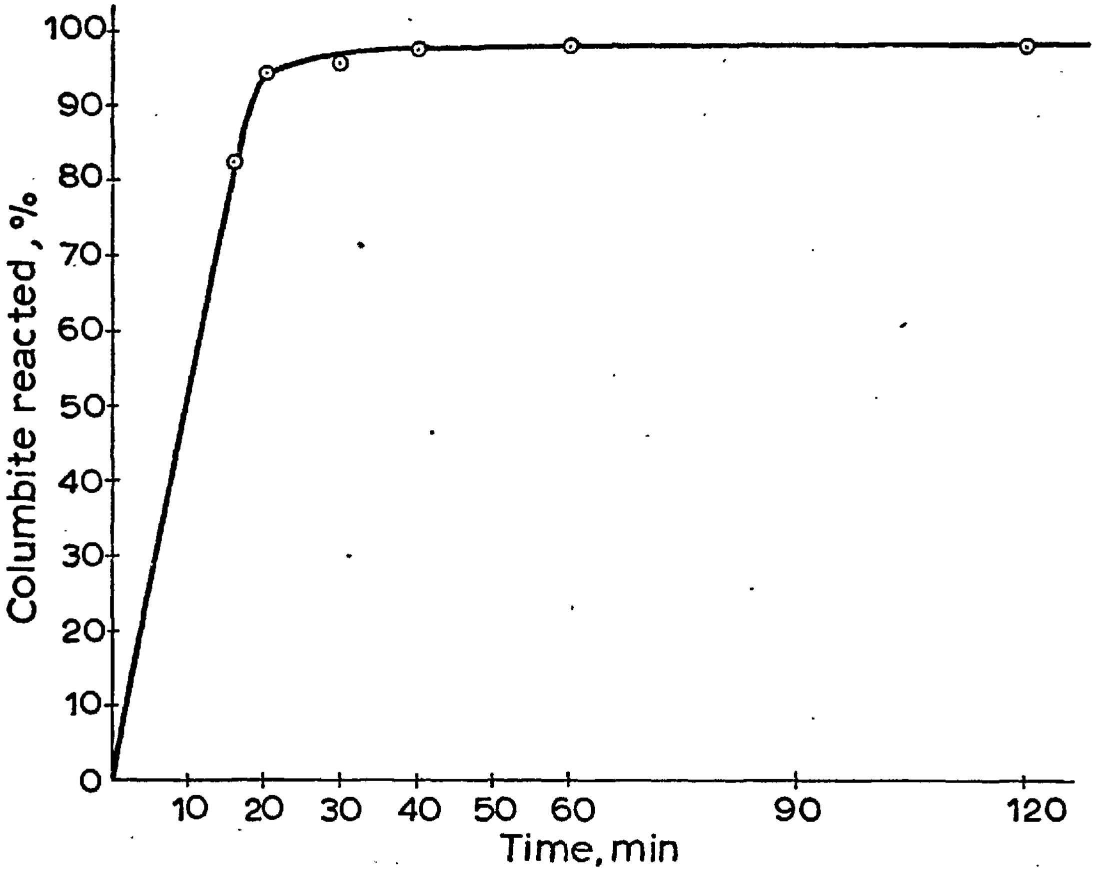


Fig. 36 Reaction of columbite as a function of residence time in the furnace preheated to 550°C.
(Size of mineral : 52/100 mesh ,NaOH /mineral = 1·2 )

$$2Fe(RO_3)_2 + 12NaOH + \frac{1}{2}O_2 = 4Na_3RO_4 + Fe_2O_3 + 6H_2O,$$

and for manganese niobate and tantalate;

$$Mn(RO_3)_2 + 6NaOH + \frac{1}{2}O_2 = 2Na_3RO_4 + MnO_2 + 3H_2O.$$

In the presence of excess sodium hydroxide the ferric oxide would be converted to sodium ferrite ($NaFeO_2$) and so the manganese dioxide to sodium manganate ($Na_2MnO_4$) in oxidizing condition.

The salts of niobium and tantalum undergo hydrolytic decomposition during the queous processing according to the following equation (26):

$$12Na_3NbO_4 + 43H_2O = 7Na_2O.6Nb_2O_5.32H_2O + 22NaOH;$$

$$6Na_3TaO_4 + 30H_2O = 4Na_2O.3Ta_2O_5.25H_2O + 10NaOH.$$

## 4. Reactivities of Other Minerals as a Function of Temperature

In addition to the qualitative information which was obtained by the D.T.A. tests, (Section 2.3, PART I) this section, together with the preceding sections, is concerned with quantitative assessment of the reactivity as a function of temperature. The minerals tested include cassiterite, xenotime, hematite, magnetite, ilmenite, chromite, garnet, and quartz.

These mineral samples were of unknown origin unless specified and they were purified by physical separation. The confirmation of the mineral species was made by means of reflected light microscopy, electron microprobe analysis or x-ray diffraction. In addition, chemical analyses were conducted where necessary.

The procedure for the reactivity tests was essentially similar to that for monazite. The mineral sample, up to 5g, was mixed with powdered sodium hydroxide from 50 to 100% in excess over the assumed stoichiometric requirement to ensure reaction. In order to minimize the time required for the tests a simplified technique was employed to evaluate the reactivity of each mineral. The method consisted of dissolution of the reaction product in water followed by settling and decantation. Since the water-insoluble reacted particles were usually fine and in suspension whereas the unreacted mineral particles were coarse and settled readily, it was possible to separate the two by repeated suspension and decantation. The final coarse solids were washed with an appropriate selective solvent, usually an acid, to ensure the removal of any reacted coating material. The dry weight of the unreacted mineral was used to calculate the percent of reaction. A wet screened size fraction of 72/200 mesh was used. This method was useful where a pure mineral and coarse sizes were encountered, however it was inadequate where finer sizes or relatively impure minerals were to be tested. In this case chemical analysis had to be employed. Some details will be given where appropriate in the following sections.

## 4.1 The reactivity of cassiterite

Samples of Odegi cassiterite in pea size was hand picked and crushed to obtain a 72/200 mesh fraction, which was further purified by gravity separation followed by magnetic and electrostatic separations. The final clean sample was not sufficiently pure (90.7% $SnO_2$) to employ the simplified technique in obtaining percentages of reaction. The fine size fraction (-300 mesh) was obtained by grinding the 72/200 mesh fraction. The results of reactivity tests are shown for two size ranges as a function of temperature in Fig. 37, from which it can be seen that the effect of size appears to be considerable (approximately 50% difference in percentage of reaction). The coarse size cassiterite did not react appreciably below 650°C, but above this temperature the reactivity increased gradually to 24% (at 770°C). The fine size cassiterite started to react at a much lower temperature (350°C), but it was incomplete even at around 800°C (81%).

## 4.2 The reactivity of chromite

A high grade of Zwartkop chromite concentrate (<1% $SiO_2$) was obtained from Dr.E.Cohen of the Department of Mining and Mineral Technology. The sample was screened to obtain the 72/200 mesh fraction and further purified by physical separation. The purified sample assayed: 45.1% $Cr_2O_3$, 13.4% $Al_2O_3$, 23.7% FeO, 5.2% MgO, 0.45% $SiO_2$ and Ti, Mn in minor quantity. A polished section of the prepared sample was examined by electron microprobe analysis and the result showed that the distribution of chromium varied from one grain to another due to substitution of Cr by other elements. Although the overall chromium content was low, the grain counting over 100 grains, based on Cr element, indicated only 4% non-chromite grains. Hence, the sample was

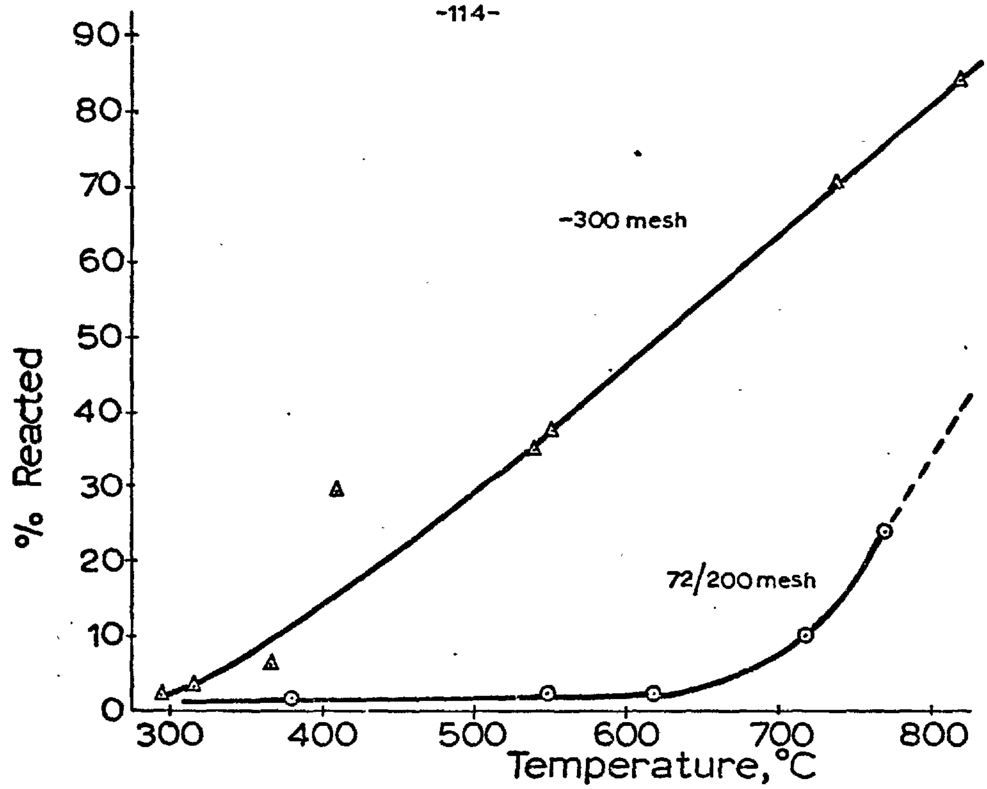


Fig. 37 Reaction of cassiterite with sodium hydroxide as a function of temperature on two size ranges. (NaOH/cassiterite = 1·0, heating for 1 hour)

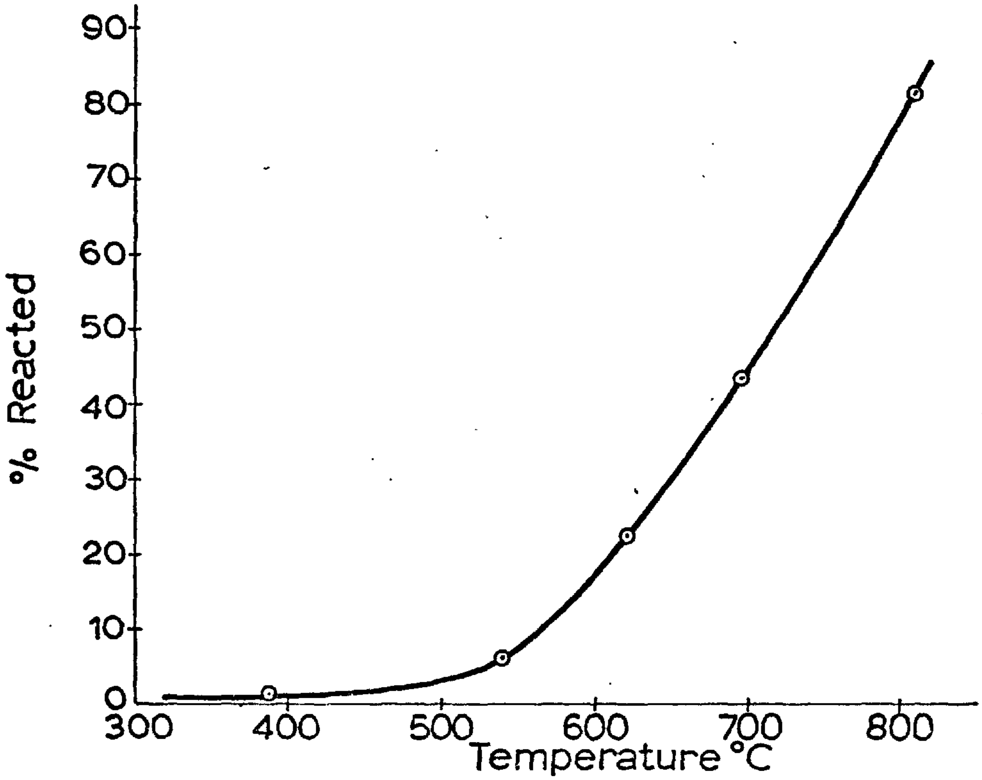


Fig. 38 Reaction of chromite with sodium hydroxide as a function of temperature. (Size of mineral: 72/200 mesh, NaOH/chromite = 1·2 heating, for 1 hour)

regarded as 96% pure chromite.

The simplified technique was used for determining the percentage of reaction.

The results obtained from the reaction tests are shown in Fig. 38. The reaction of chromite with sodium hydroxide initiated at around 500°C and its reactivity gradually increased. The reaction was still incomplete and amounted to 80% at 810°C. The reaction products were all in a fused state, yellow in colour, which is due to the sodium chromate formed. No frits were obtained within the heating periods and temperatures studied.

## 4.3 The reactivity of ilmenite

A coarse grained ilmenite ore was crushed to liberate ilmenite from the associated gangue minerals and it was carefully sized to facilitate physical separation. The 72/200 mesh fraction was cleaned successively by a permanent magnet and a disc type magnetic separator (of higher intensity). Examination of a polished section of the purified sample showed that the distribution of titanium and iron was generally uniform throughout the grains with a similar level of element content in all grains. The assay results gave 48.4% $TiO_2$ and 48.9% FeO. The ratio of Fe/Ti was slightly higher (1.31) than the theoretical value (1.17). The excess iron may be due to the minute needle-like exsolved hematite grains in most of the ilmenite grains which the electron-probe microanalyser detected. Such impurity is unavoidable in natural ilmenite. The simplified technique was used in evaluating the reactivity of the mineral. The results of reaction tests are shown in Fig. 39 as a function of temperature. The reaction initiated at around 500°C but the rate was a slow one: only a few percent of the mineral reacted during 1 hour heating. Complete decomposition of the mineral was achieved above 800°C within the same period of time. The reaction

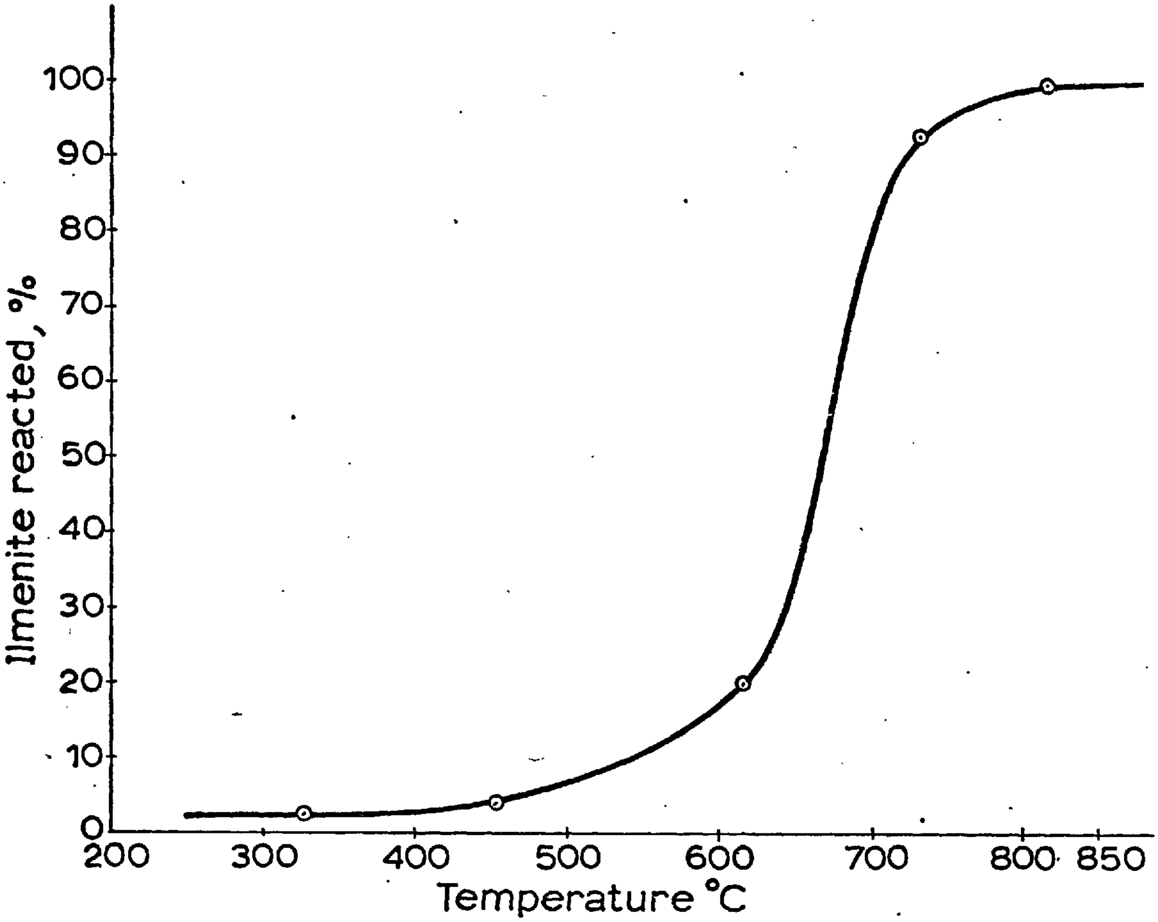


Fig. 39 Reaction of ilmenite with sodium hydroxide as a function of temperature. (Size of mineral: 72/200 mesh, NaOH/ilmenite = 1·2, heating for 1 hour)

product after heating to this temperature had not fused but was a hard porous mass, which gave relatively ready dissolution in water than a totally fused one.

## 4.4 The reactivity of iron oxide minerals

### 4.4.1 Hematite

Coarse crystalline Swedish hematite lumps were crushed and hand picked. The picked hematite was ground and wet screened to obtain 72/200 mesh fraction which was further purified by magnetic separation. A portion of this sample was ground to pass 300 mesh and kept for use in fine size tests. Chemical assay of the purified sample gave 97.2 % $Fe_2O_3$. In obtaining percentages of reaction the simplified method was employed for the coarse size, for the fine size tests, however, this method was inadequate. For the purpose of evaluation of the simplified method three different points were compared with the results based on the chemical determination. The result was that the reaction percent by the simplified method gave an average of 2% greater than the method based on iron determination. This was probably due to the impurity mineral of higher reactivity such as quartz or a silicate mineral which was present in minor quantity in the sample. Silicious gangue minerals showed relatively higher reactivity than iron oxide minerals (see D.T.A. results on siliceous minerals, Section 2.3, PART I)

The results for the reaction of hematite are shown for two different size fractions in Fig. 40. The coarse size hematite did not react below 400°C, but above this temperature the extent of reaction in a fixed time increased steadily with the temperature. The reaction was still incomplete (74%) at the highest temperature tested (820°C). Fine size hematite started to react at 200°C but the reaction did not exceed 25% until the temperature was raised to about 350°C, beyond which the reactivity

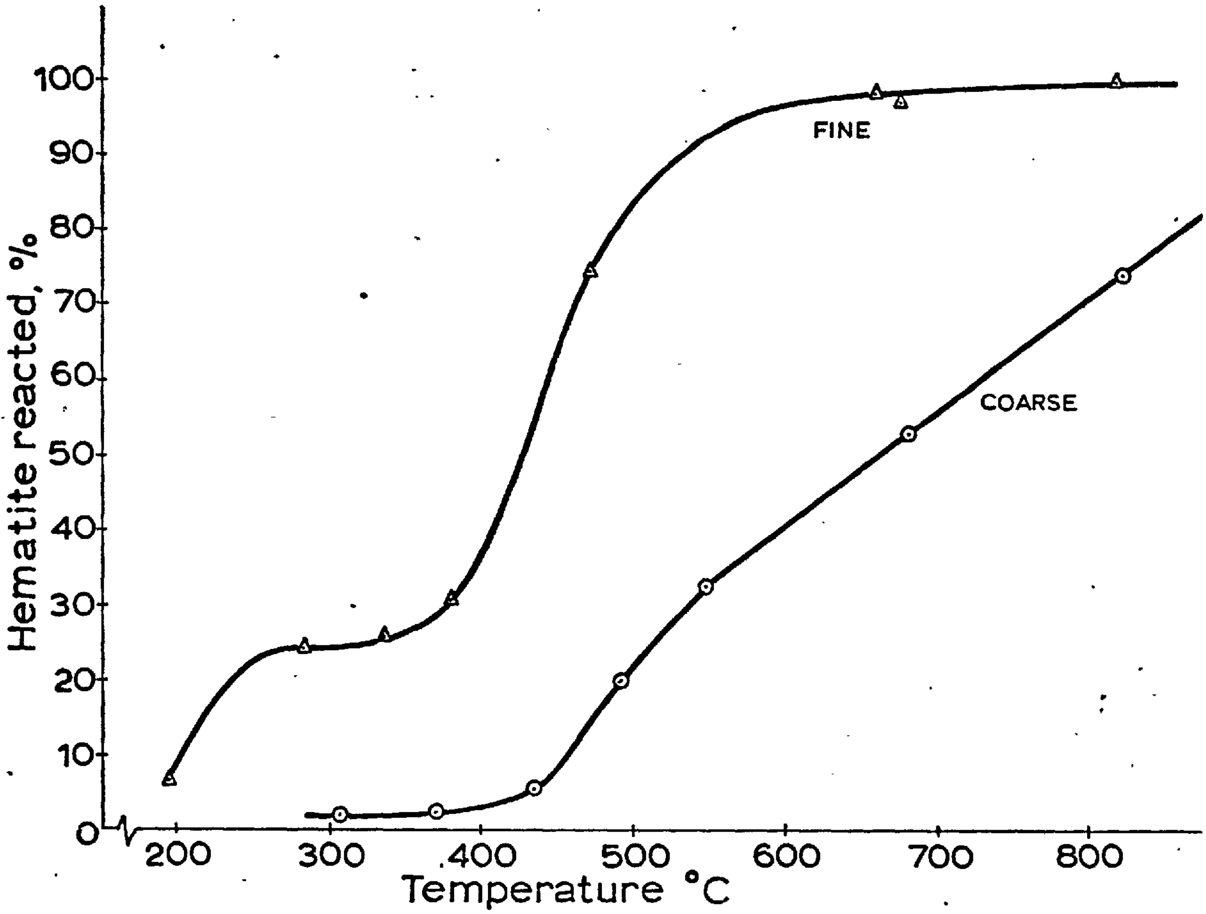


Fig. 40 Reaction of hematite with NaOH as a function of temperature on two size ranges (72/200, -300 mesh) (NaOH/hematite (wt) = 0·75, heating for 1 hour)

rose sharply. Almost complete reaction was obtained at 650°C.

### 4.4.2 Magnetite

A clean magnetite sample was prepared from a high grade concentrate by further physical purification i.e. repeated wet magnetic separation followed by demagnetization. The purified 72/200 mesh fraction was used for the reactivity tests. The chemical assay of the sample gave 63.5% Fe (Theo. 72.4% Fe). The purity was such(87.6% magnetite) that the simplified method was not applicable even for the coarse size and the percentages of reaction were calculated from the chemical determination of iron content.

The results are plotted as a function of temperature for the two sizes in Fig. 41. Magnetite showed lower reactivity than hematite. The extent of reaction of the coarse magnetite did not exceed 10% below 600°C (460°C on hematite) and a temperature high as 820°C (660°C on hematite) was required to obtain 50% reaction. To a similar extent as hematite, the reactivity of fine magnetite was greater than the coarse.

## 4.5 The reactivity of Xenotime

A sample of commercial xenotime concentrate was obtained from Mr I.C.Schomburgk, National Research Development Corporation, London. S.W.1. The sample contained approximately 20% of impurity minerals such as zircon, monazite and minor quantities of weakly magnetic iron minerals. The available physical separation methods such as gravity separation, magnetic and electrostatic separation did not improve the purity appreciably. The assay of the cleaned sample showed 31.4% $Y_2O_3$, 17.7% $P_2O_5$. The simplified method of determining percentages of reaction was not used for this mineral because of the impurity content. The assay values of yttrium were used for calculating the percentage of reaction. The determination of the yttrium

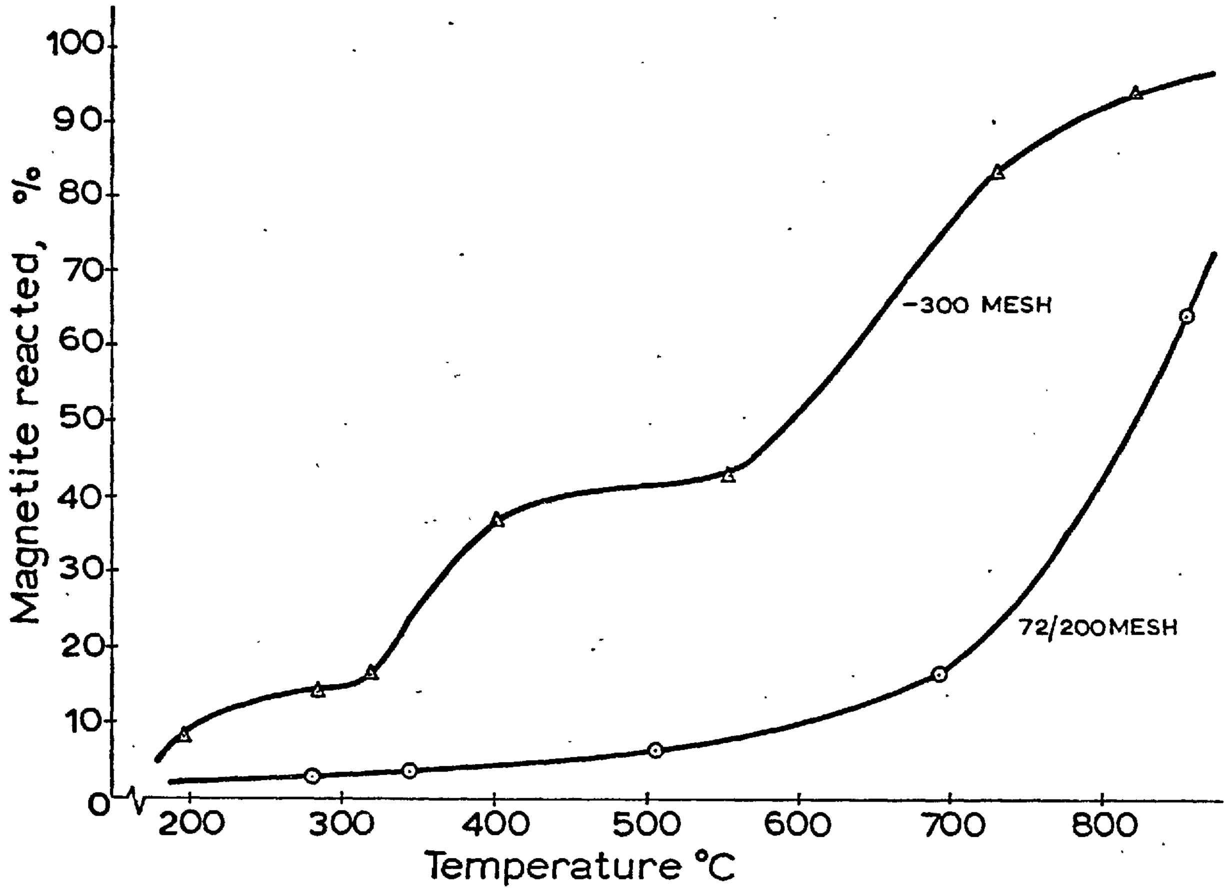


Fig. 41 Reaction of magnetite with NaOH as a function of temperature on two size ranges (72/200, -300 mesh) (NaOH/magnetite = 0·75, heating for 1 hour)

content was obtained by x-ray fluorescence spectroscopy conducted by Mr J. Mills, Analytical Services Section, Imperial College.

The results are plotted in Fig. 42 as a function of temperature, from which it can be seen that most of the mineral reacted around 300°C but complete reaction was achieved around 400°C. All the products obtained below 400°C were in a form of porous aggregates (see colour photograph, Fig. 22D) whereas the products at higher temperatures formed a fused mass. As was indicated by the D.T.A. thermogram, this was probably caused by the melting of the product phase. Also, it was observed that the residual unreacted mineral after heating to 400°C were of 95% zircon, quantitatively unattacked.

## 4.6 The reactivity of siliceous minerals

### 4.6.1 Quartz

Lumps of crystalline quartz were crushed and screened for hand sorting. The hand picked quartz was ground to obtain 52/200 mesh fraction, which was further purified by gravity separation and high intensity magnetic separation. The sample was cleaned with hot hydrochloric acid to remove any carbonaceous impurity. The final, washed, sample was rescreened wet, to obtain the 72/200 mesh fraction which was dried and used for the reactivity tests. The mineral was sufficiently pure to employ the simplified technique in obtaining percentages of reaction after heating. The results of the tests are shown in Fig. 43 as a function of temperature. As was predicted from the D.T.A. test the extent of reaction increased sharply at 280°C as with a number of other minerals. The product of reaction was white in colour and in a dry powdery state, completely soluble in water.

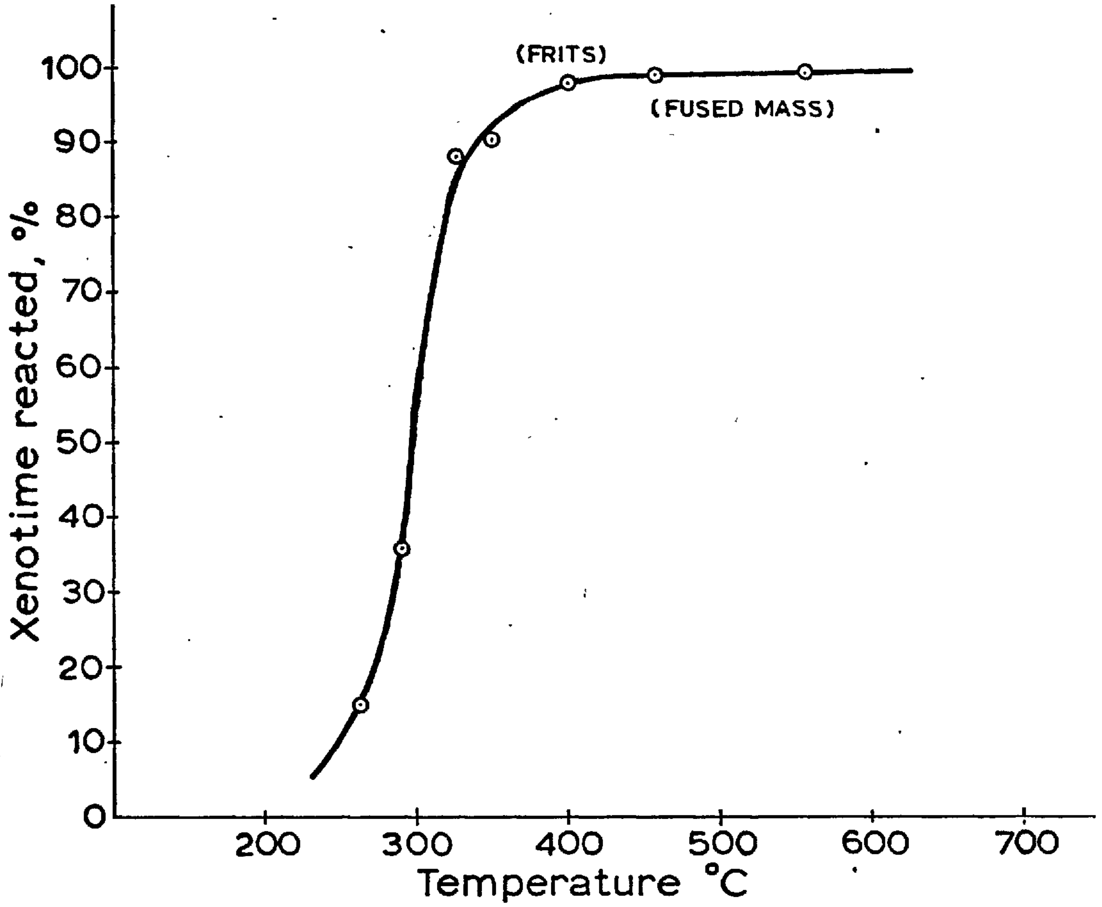


Fig. 42 Reaction of xenotime as a function of temperature. (Na OH/xenotime = 1·5, heating for 1 hour)

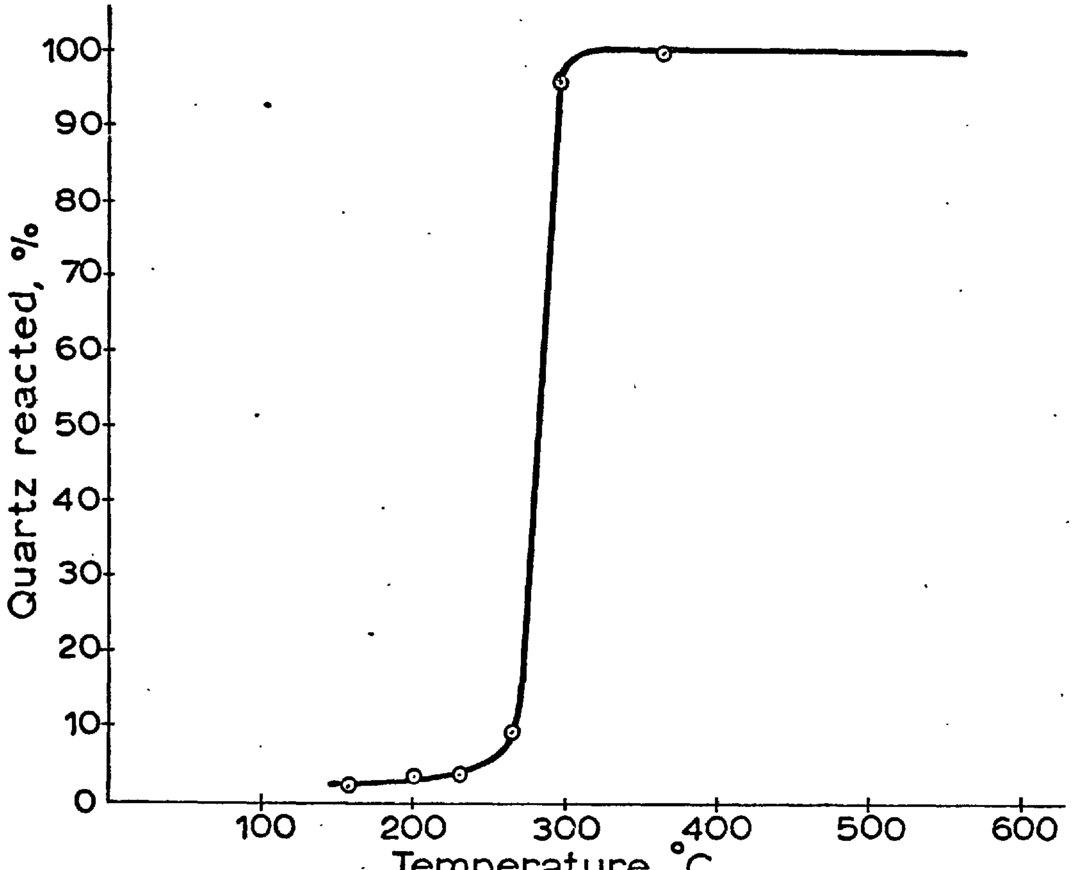


Fig. 43 Reaction of quartz with sodium hydroxide as a function of temperature. (Size of quartz: 72/200 mesh, NaOH/quartz = 2·6, heating for 1 hour)

### 4.6.2 Garnet

A high grade sample of commercially available abrasive garnet (52 mesh) was purified by means of dense liquids followed by magnetic and electrostatic separation. The cleaned sample was ground and screened wet to obtain the 72/200 mesh fraction.

Garnet is a complex silicate and occurs in nature in many varieties. The ultimate identification of the mineral is not a simple task and for present purposes it was not necessary, nevertheless observation of the physical properties such as colour (red), hardness (>quartz) and specific gravity (3.8) together with chemical information obtained by an electron-probe microanalyser lead to the conclusion that the mineral was a variety of almandite ($3FeO.Al_2O_3.3SiO_2$).

The results of the reactivity tests are shown in Fig. 44. The reaction first became apparent below 300°C and 50% of the mineral reacted in an hour at 360°C. Complete reaction was achieved within an hour at above 550°C. The products of complete reaction were porous brown frits.

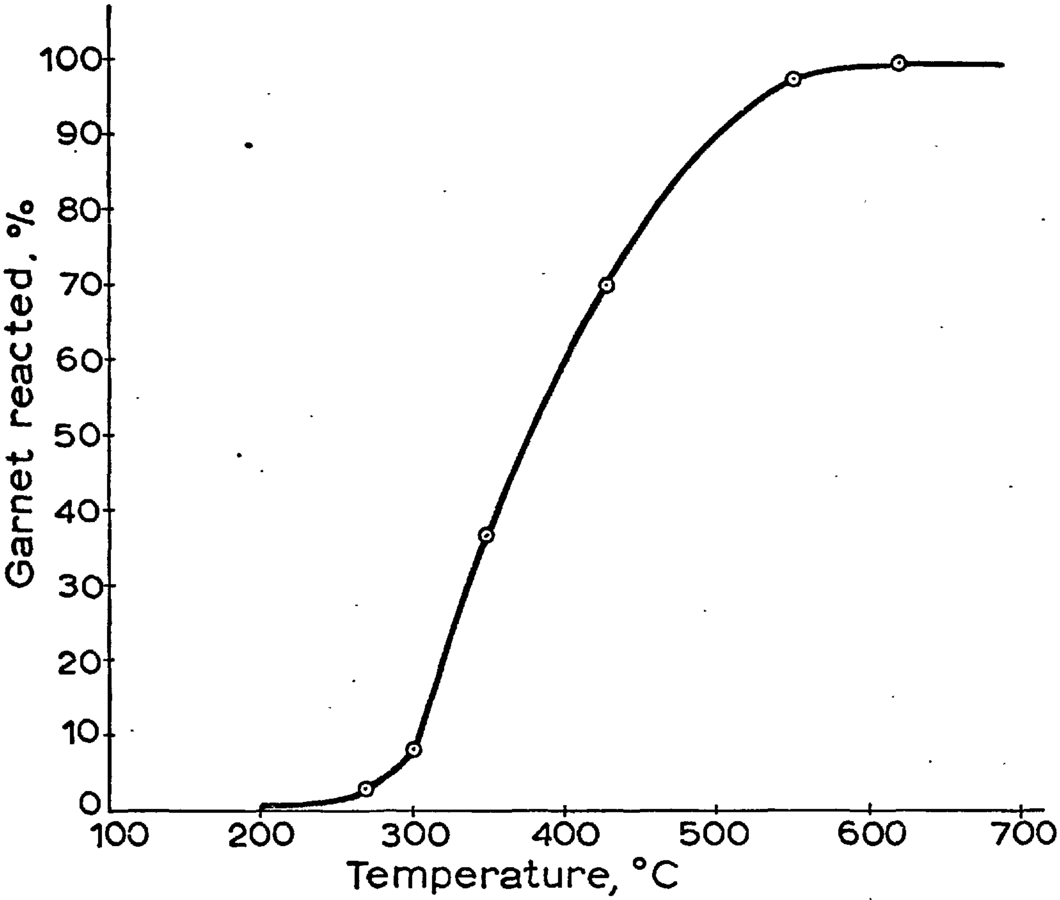


Fig. 44 Reaction of garnet with sodium hydroxide as a function of temperature.
(Size of mineral : 72/200 mesh, NaOH/garnet = 1·5, heating for 1 hour)

## 5. Selective Reaction

In the previous section it has been pointed out that the current methods of physical separation are not adequate for treating some pairs of minerals due to the similarity of their physical properties. Mixtures of interlocked minerals also cannot be separated by physical methods.

Chemical processing prior to separation is a possible alternative for these materials if one of the materials can be preferentially reacted leaving the other as unreacted solid. In order to react one mineral preferentially it is important to know the conditions for selective reaction. For this purpose a wide range of information on the reactivities of the individual minerals is required. Such information as the influence of temperature, time, size of particles and the ratio of the reagent to mineral would be useful. Among them the reactivity in terms of temperature is most important, hence Fig. 45 has been prepared. It gives this information for a number of economic minerals as well as their associated gangue minerals. The reactivities of individual minerals of similar size range of particles (72/200 mesh) are given in terms of temperature at a fixed period of reaction (1 hour).

Examination of the data indicates a number of possibilities for selective reaction. Most of the siliceous gangue minerals and phosphate minerals react at relatively low temperatures (around 300°C) whereas some of the economic minerals such as cassiterite, chromite, ilmenite, etc. react at higher temperatures, hence the gangue minerals can be selectively reacted. Often the unit price of a concentrate (price quoted for each percent of the valuable constituent) is increased with its increased content. An intermediate cassiterite concentrate with interlocked siliceous gangue minerals, which is unsaleable due to its low metal content, could be up-graded by removing

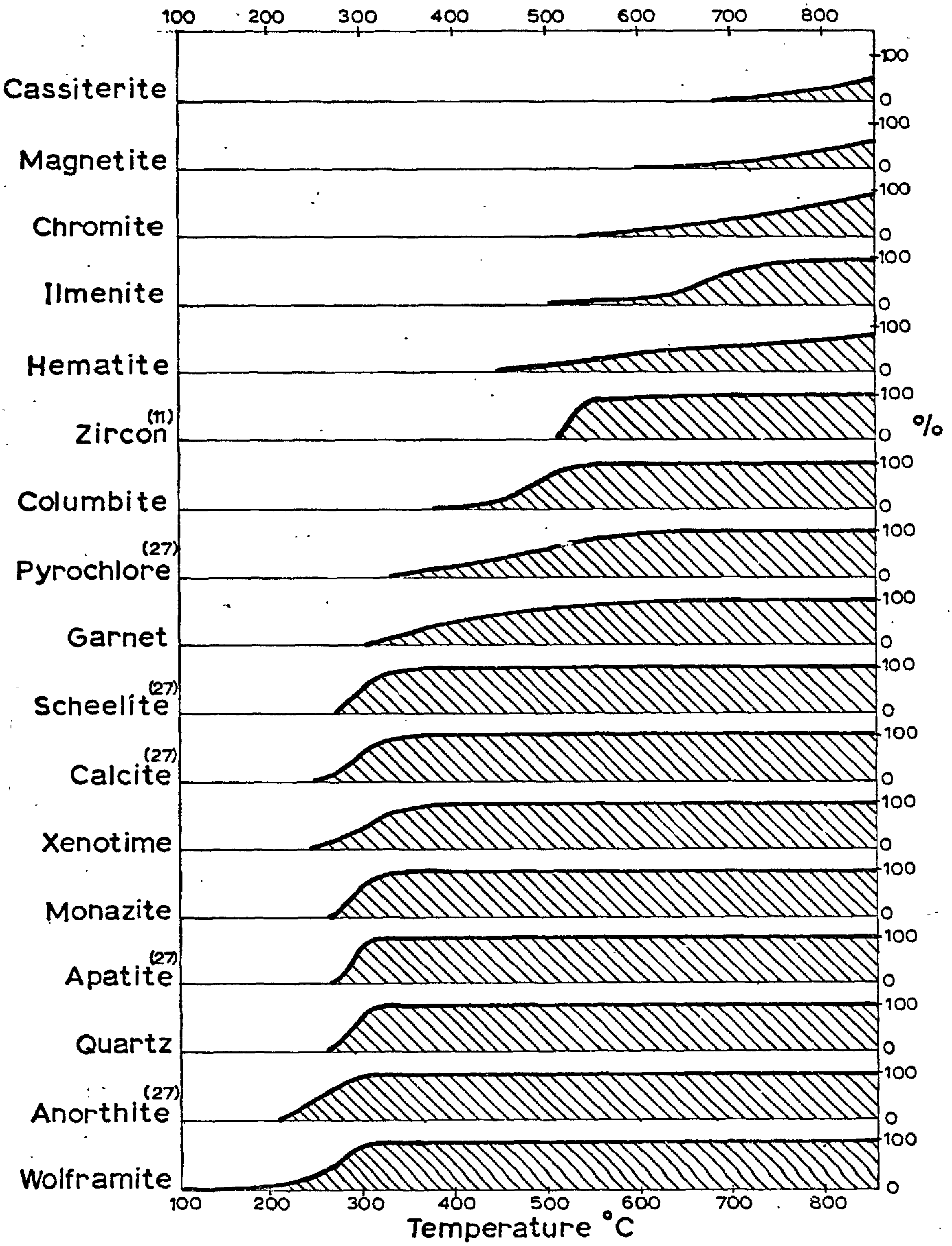


Fig. 45 Reactivities of minerals with sodium hydroxide as a function of temperature. (72/200 mesh)

the impurity by selective reaction at around 400°C. Phosphorus in iron ore is a highly detrimental impurity and sometimes an ore containing a high iron content becomes worthless due to the presence of this element. This kind of ore could perhaps be processed by this method.

The process of separating minerals by selective reaction with sodium hydroxide has an advantage over any physical separation process in that the separation and the first stage of chemical processing of one of the minerals (decomposition of the mineral, see early part of general introduction) are accomplished in the one operation. One of the separated products is already in a refined state that it can be readily converted into saleable industrial chemicals or further purified. However, the cost of the process is mainly governed by the cost of the reagent, which is relatively expensive, hence those minerals to be treated by the alkali process should have at least a moderately high value. Minerals such as cassiterite, wolframite, columbite,, monazite and xenotime qualify in this respect. A mixed material which consists of two high value minerals with a high content of the value is sometimes unsaleable if they are not separated. Such a case is found in practice, for example, a mixed concentrate of wolframite and cassiterite for which physical methods are ineffective. Processing of the material by reacting wolframite selectively with the caustic alkali yielding two separate high value saleable products is considered to be suitable.

In the following sections some possibilities of processing mineral pairs are described with the pairs: wolframite and cassiterite, xenotime (or monazite) and zircon, columbite and cassiterite, and apatite with iron oxides as particular examples. Some experimental work is discussed in which a particular mixed concentrate of wolframite and cassiterite was processed successfully.

## 5.1 Selective reaction of wolframite and cassiterite.

Wolframite and cassiterite possess similar physical properties: the densities are 7 - 7.5 (wolframite) and 6.8 - 7.1 (cassiterite), and both minerals are weakly magnetic. The practical failure of the physical methods of separation can be seen in an intermediate concentrate containing high percentages of both wolframite and cassiterite, which has been rejected from the physical processing plant of South Crofty Limited.

The individual reactivities of these two minerals with solid sodium hydroxide differed greatly (see Fig. 31 and 37): wolframite reacted completely at 350°C whereas the reaction of cassiterite was still incomplete even at a temperature as high as 800°C. Thus there is a possibility of processing the mixed concentrate by reacting wolframite selectively and leaving cassiterite unreacted (see Fig. 46).

### 5.1.1 Selective reaction tests on the mixed tungsten-tin concentrate from South Crofty Ltd.

Description of the ore - The sample of mixed tungsten-tin concentrate was obtained from Dr. E. Cohen, Department of Mining and Mineral Technology, and it contained a high percentage of tungsten (26.2%) as wolframite and tin (12.6%) as cassiterite, together with metallic iron and iron oxides (total iron 19%). The size distribution of the sample is shown in Table 16.

From the results of the reactivity tests on the individual constituent minerals which are shown in Fig. 46, it was estimated that the probable optimum temperature was between 320 and 350°C.

Test Results

A series of tests for selective reaction was carried out in which the weight ratio of sodium hydroxide to concentrate was varied. The sample was mixed with sodium hydroxide and heated to

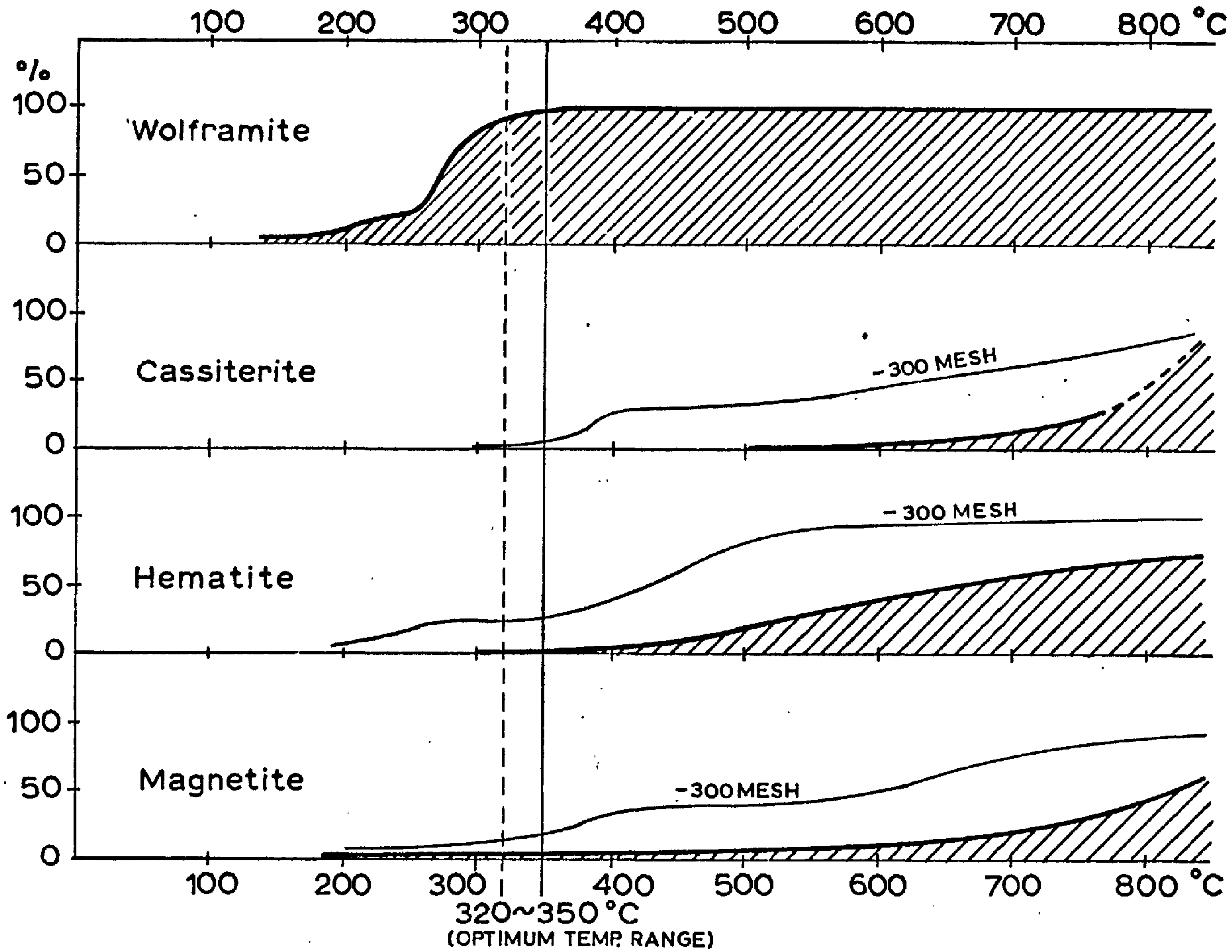


Fig. 46 Reactivity of major mineral constituents in the mixed W/Sn concentrate with Na OH — shows optimum temperature for selective reaction of wolframite from cassiterite and Fe-oxides.

Table 16. Size distribution of the mixed tungsten-tin concentrate from South Crofty Ltd.

| Mesh, B.S. | Wt. % | Cumulative wt.% retained |
|---|---|---|
| + 36 | 1.9 | 1.9 |
| 52 | 2.4 | 4.3 |
| 72 | 8.9 | 13.2 |
| 100 | 15.8 | 29.0 |
| 150 | 20.7 | 49.7 |
| 200 | 17.2 | 66.9 |
| 300 | 11.3 | 78.2 |
| -300 | 21.8 | |
| Total | 100.0 | |

320°C for an hour. All the reaction products from the tests were greenish blue in colour and in the form of loose aggregates which disintegrated readily during the subsequent treatment with water. The residue was filtered and washed again with water. Thus the reaction products were split into two products: the solution containing tungsten (as sodium tungstate) and the residue containing unreacted cassiterite and precipitated iron oxides. The respective products were assayed for tungsten and tin. The results obtained are shown in Fig. 47 in terms of the recovery of the major constituents concerned. In all cases the recovery of tin and tungsten was above 80%. As expected, the recovery of tungsten was increased with a greater ratio of sodium hydroxide to concentrate, whereas the recovery of tin showed the adverse effect. The best result was when the ratio used was 1 : 1. In this case the recovery of tungsten in the solution was 95.4 % and that of tin in the leach residue was 94.8%. In other words, an effective separation was achieved by heating the mixture of ore and sodium hydroxide in 1 : 1 weight ratio to 320°C for 1 hour followed by water leaching.

Further information relating to the tests is tabulated in Table 17 where weight distributions of the separated products and their grades are shown. Since the tungsten product was obtained in solution, the concentration of which may vary according to the quantity of wash water, the dry weight of the water-soluble portion of the reaction product was used as the basis for calculation.

The tungsten could be treated directly for the recovery of tungstate or $WO_3$. The leach residue containing tin could be treated as a tin concentrate or further up-graded by a physical separation method such as tabling or in a hydrocyclone by which the bulk impurities present as finely divided iron and manganese oxides can be readily removed from the relatively

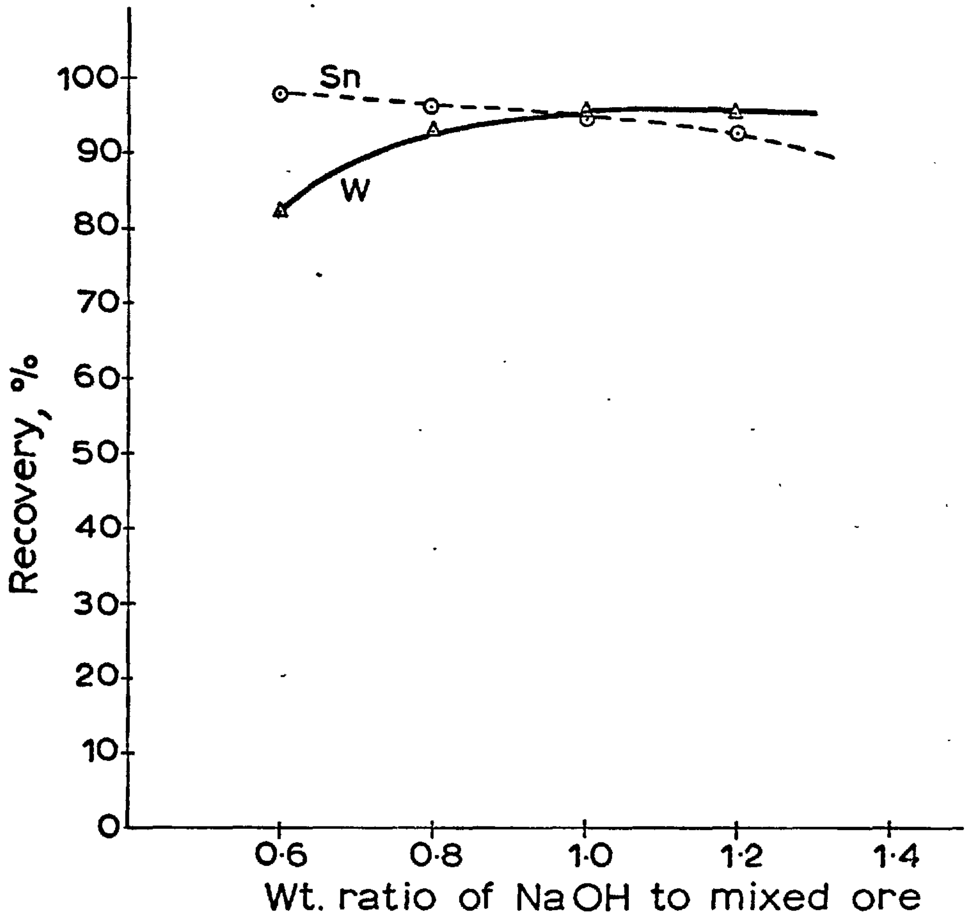


Fig. 47 Results of selective reaction tests on the mixed W/Sn concentrates with sodium hydroxide at 320°C for 1 hour.

Table 17. Results of selective reaction tests on South Crofty tungsten-tin mixed Concentrates. (Heated to 320°C for 1 hour.)

| Test No. and NaOH/ore (wt. ratio) | Product of Separation | Product Weight % | Assay | | |
|---|---|---|---|---|---|
| | | | % W | % Sn | % Fe |
| W/Sn-6<br>0.6 | Leached Portion[*] | 51.1 | 27.6 | 0.3 | - |
| | Residue | 48.9 | 6.3 | 16.5 | - |
| W/Sn-7<br>0.8 | Leached Portion | 58.5 | 24.3 | 0.4 | - |
| | Residue | 41.5 | 2.2 | 16.2 | - |
| W/Sn-8<br>1.0 | Leached Portion | 63.2 | 20.7 | 0.5 | 0.0 |
| | Residue | 36.8 | 1.7 | 16.4 | 27.4 |
| W/Sn-9<br>1.2 | Leached Portion | 67.1 | 17.6 | 0.6 | - |
| | Residue | 32.9 | 1.9 | 17.3 | - |

---

[*] Leached portion = Reaction product - Residue after water-leaching.

coarse unreacted cassiterite. The reacted iron and manganese oxides are probably highly reactive so that some chemical method such as acid washing after gravity or size separation would lead to a high grade of cassiterite concentrate.

## 5.2 Selective reaction of columbite and cassiterite

Again, like wolframite and cassiterite, these two minerals have similar physical properties. They occur together in a Nigerian deposit and complete separation is difficult (28)(29). Selective reaction with sodium hydroxide may be achieved by choosing a suitable temperature of reaction. From Fig. 44 it can be seen that coarse columbite completes its reaction at 540°C whereas cassiterite initiates its reaction at 670°C. The optimum temperature for the selective reaction clearly would be 540°C. However, difficulty may be encountered in separating the products after reaction since sodium niobate and tantalate are not water soluble.

No testwork has been carried out with this pair of minerals but the products could possibly be separated by physical methods such as tabling or any sizing techniques. The proposed processing scheme is therefore:

1. Reaction with sodium hydroxide at 540°C for 1 hour (optimum conditions for columbite).

2. Leaching with water:- removal of excess sodium hydroxide and other soluble forms of product such as sodium manganate.

3. Acid leaching of the residues in concentrated hydrochloric acid:- removal of iron manganese oxides.

4. The residues may now contain niobic-tantalic acid as fine solids with coarse unreacted cassiterite (cassiterite is insoluble in hydrochloric acid) and can be fed to a concentrating table or any other sizing equipment; or the Nb/Ta portion dissolved

in HF (cassiterite is insoluble). A proposed flow sheet is given in Fig. 48.

## 5.3 Selective reaction of xenotime (or monazite)and zircon

The bases of the physical methods for separating these minerals are the magnetic and electrostatic properties. In practice, however, the separation is incomplete.

The feasibility of processing the mixed minerals is good since monazite and xenotime react completely below 400°C but zircon does not start to react until >500°C. Hence, zircon can be separated by reacting only monazite and/or xenotime at 400°C followed by water leaching. The product of water dissolution will contain all the phosphates in solution ($Na_3PO_4$), finely dispersed rare earth oxides, and unreacted zircon sands. After solid-liquid separation the sodium phosphate can be recovered from the solution and the residues may be washed over a fine screen to separate the fine rare earth oxides from the relatively coarse unaltered zircon. The product of this process usually gives the rare earth oxides as particles of size 2-3μm, which will readily pass through an industrial fine screen. An alternative method may be separation by a concentrating table where the fine oxide suspension can be washed away from the zircon sands. No practical test work has been directly carried out, however, reaction tests with monazite and xenotime containing some zircon impurity below 400°C indicated that all the zircon in them remained quantitatively as unreacted particles. A proposed flow sheet for processing this type of mixed concentrate is given in Fig. 49.

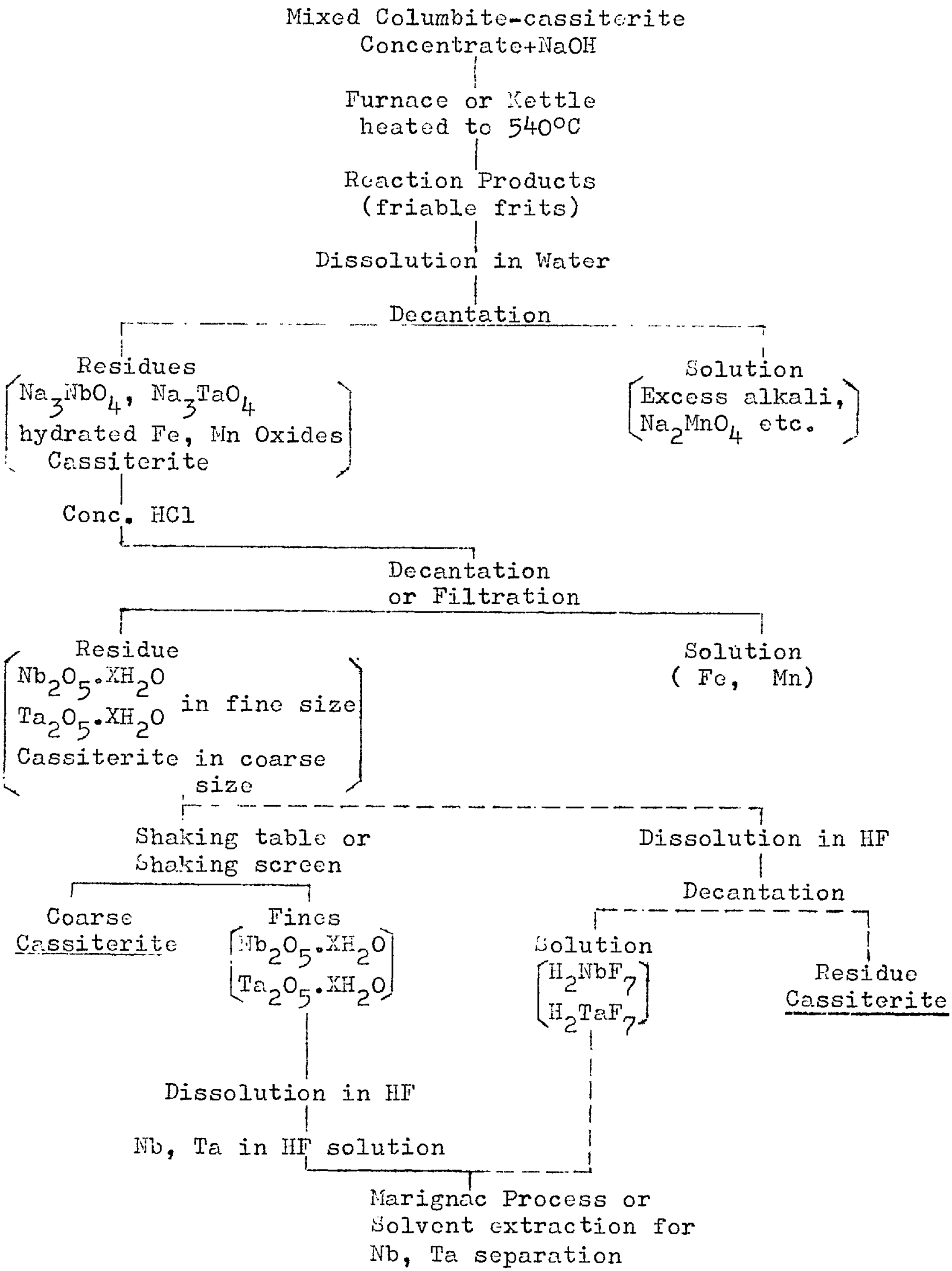


Fig. 48. A proposed Flowsheet for Processing of Columbite-Cassiterite mixture.

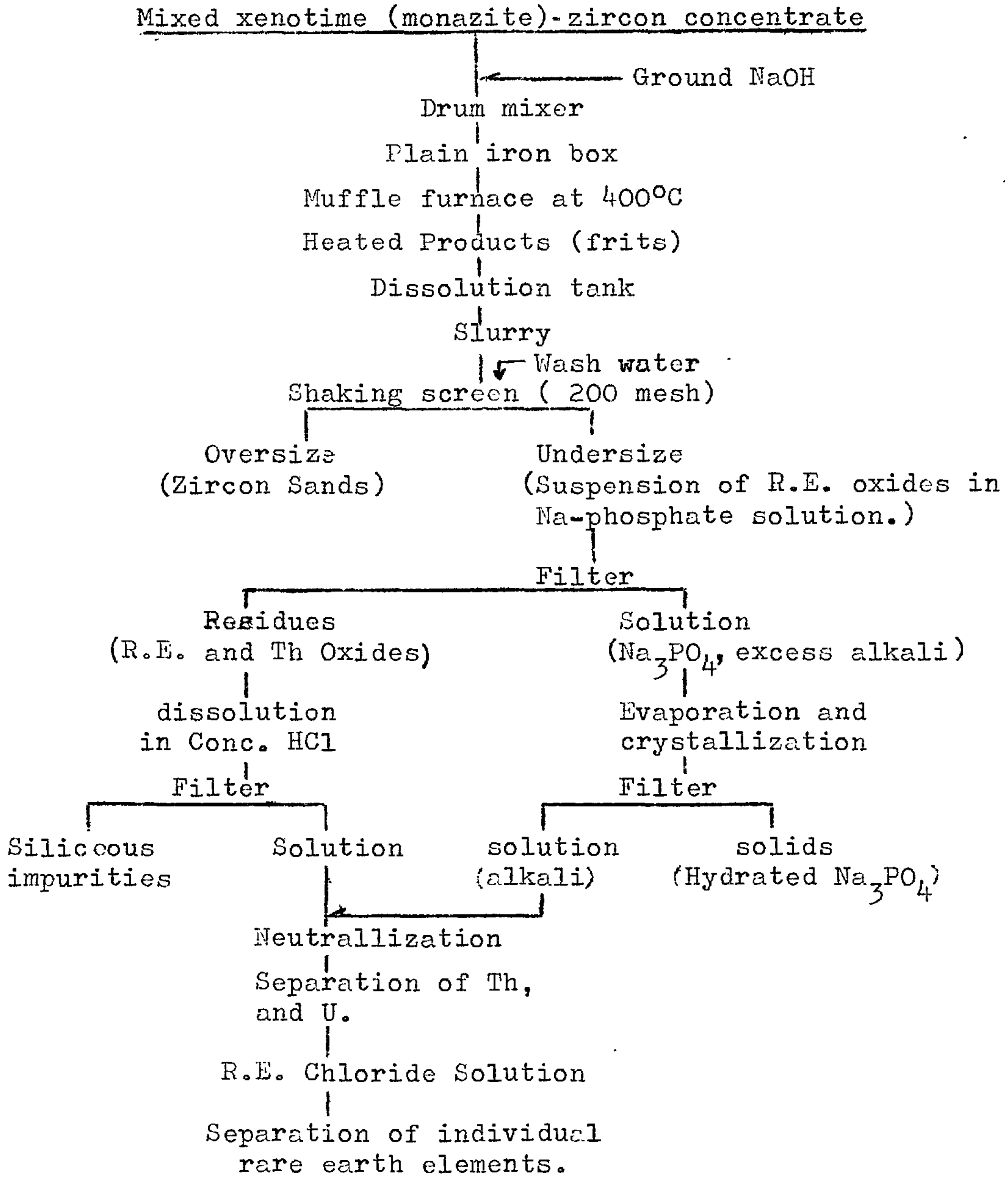


Fig. 49. A proposed flowsheet for processing mixed concentrate of xenotime (monazite) - zircon mixture.

### 5.4 Apatite-iron oxide minerals

An apatite ore such as from Sukulu(30) contains finely disseminated iron oxides. Concentration of this ore is carried out by washing the mined ore to reject clayey materials followed by magnetic separation where the most of the coarse grained iron oxides are removed. Further concentration is conducted by flotation where apatite is floated using fatty acids as collector. As the apatite is coated with an iron oxide layer the selectivity of separation is usually low. (The buyers specify the total of Fe, Al oxides less than 3% or in some cases, lower than 0.5%).

This type of intermediate apatite concentrate with considerable iron content can be directly processed chemically without further physical concentration by reacting the mineral with sodium hydroxide. From Fig. 45 it can be seen that apatite reacts completely at moderately low temperature (around 300°C). Thus, the apatite can be converted into soluble sodium phosphate leaving the iron behind as insoluble oxide and the phosphate can be recovered from the water leach solution. However, practical difficulty may arise during the water leaching operation because of the reverse reaction,

$$3Ca^{2+} + 2PO_4{}^{3-} \rightarrow Ca_3(PO_4)_2.$$

It is essential to convert the calcium to an insoluble form. This could be achieved by either of the following methods:

a. Treatment of the reaction product by $SO_3$ or $CO_2$ gas before water leaching to convert the calcium oxide formed into either insoluble $CaSO_4$ or $CaCO_3$,

b. Addition of excess silica in the reaction mixture before heat-treatment to combine with the calcium as $Ca_2SiO_4$.

The reaction products of apatite and solid sodium hydroxide at 300°C are in the form of porous aggregates and, as such are readily amenable to gaseous treatment. The calcium sulphate

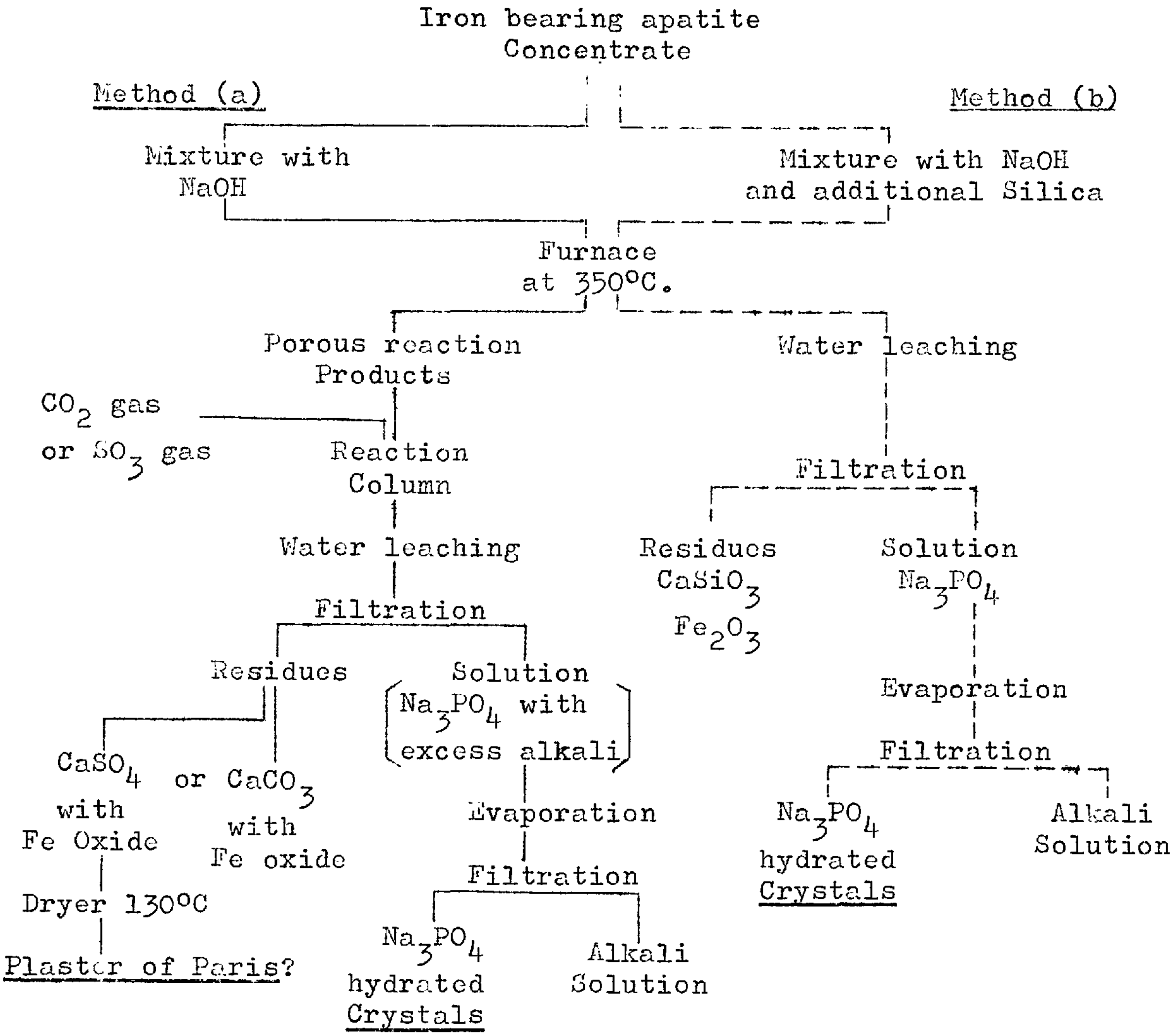


Fig. 50 Proposed flowsheet for processing of iron bearing apatite concentrates.

obtained in the first instance could perhaps be used for production of plaster of Paris. The method (b) is based on the fact that most ore contains some silica as quartz or silicates which react readily with sodium hydroxide and consume the reagent but this can be utilized as combining agent for the calcium as water-insoluble calcium silicate. The quantity of silica necessary would be adjusted to the ore treated. No test work has been carried out to confirm the possibilities, although the thermodynamic conditions are favourable (see Table 18). The suggested processing methods are diagramatically presented in Fig 50.

## 5.5 Processing of scheelite by solid alkali

The direct decomposition of scheelite concentrates with hydrochloric acid is widely used in industrial practice, although treatment by sodium carbonate is also used. In the acid process,(5) the finely ground ore is heated with concentrated hydrochloric acid for 6 to 8 hours at 70 to 80°C. With stirring in an iron reactor lined with rubber or some other acid resistant material. Approximately 250% of the stoichiometric amount of the acid and a small quantity of nitric acid are consumed in the process.

In the alkali carbonate process two methods are used: fusion and aqueous leaching.(31) The fusion method is carried out in a rotary furnace at 800 to 900°C. The consumption of alkali is very high: 317% or more of the stoichiometric amount is required in the charge to ensure a satisfactory leaching of tungsten. When quartz sands are present in the charge the addition of sodium carbonate is reduced to a range of 50 to 100% excess over the theoretical amount. The aqueous sodium carbonate solution method employs an autoclave heated to 200°C in which 250 to 450% over the theoretical quantity of sodium carbonate is used depending on the grade of scheelite ore.

Table 18. Thermodynamic calculation on the relevant reactions in the treatment of Ca-mineral.

$CaO_{(c)} + CO_{2(g)} = CaCO_{3(c)}$

$\Delta G^{o}_{298^{o}K} = -31.1$ kcal

$CaO_{(c)} + SO_{3(g)} = CaSO_{4(c)}$

$\Delta G^{o}_{298^{o}K} = -82.6$ kcal

$CaO_{(c)} + SiO_{2(c)} = CaSiO_{3(c)}$

$\Delta G^{o}_{600^{o}K} = -21.5$ kcal

$2CaO_{(c)} + SiO_{2(c)} = Ca_2SiO_{4(c)}$

$\Delta G^{o}_{600^{o}K} = -30.9$ kcal

$\Delta G^{o}_{298^{o}K}$ for $CaCO_3 = -269.78$ k cal
" $CaSO_4 = -315.56$ "
" $Ca_3(PO_4)_2 = -929.7$ k cal

$\Delta G^{o}_{600^{o}K}$ for $Na_2SiO_3 = -353.3$ k cal
" $CaSiO_3 = -341.7$ k cal
" $Ca_2SiO_4 = -488.3$ k cal

Thus, high consumption of the reagent, long reaction period even with finely ground ore, and considerably high temperatures, particularly in the fusion method, are employed.

The reaction of scheelite with solid sodium hydroxide gives complete reaction with 1:1 weight ratio of sodium hydroxide to scheelite (360% stoichiometric amount) * at 350°C in an hour without fusing the reaction mass.(27)

No treatment of scheelite with sodium hydroxide has been reported. The reason may be due to the reverse reaction in the leaching stage:

$$CaWO_4 + 2NaOH = Na_2WO_4 + Ca(OH)_2$$

nevertheless, it may be possible to process the mineral by this method by addition of silica in the charge or treating the products with $CO_2$ or $SO_3$ as was suggested for apatite in the previous section (5.4).

A suggested flowsheet for the processing is given in Fig.51.

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* This does not imply the optimum quantity. It could be reduced, however, no further tests have been carried out.

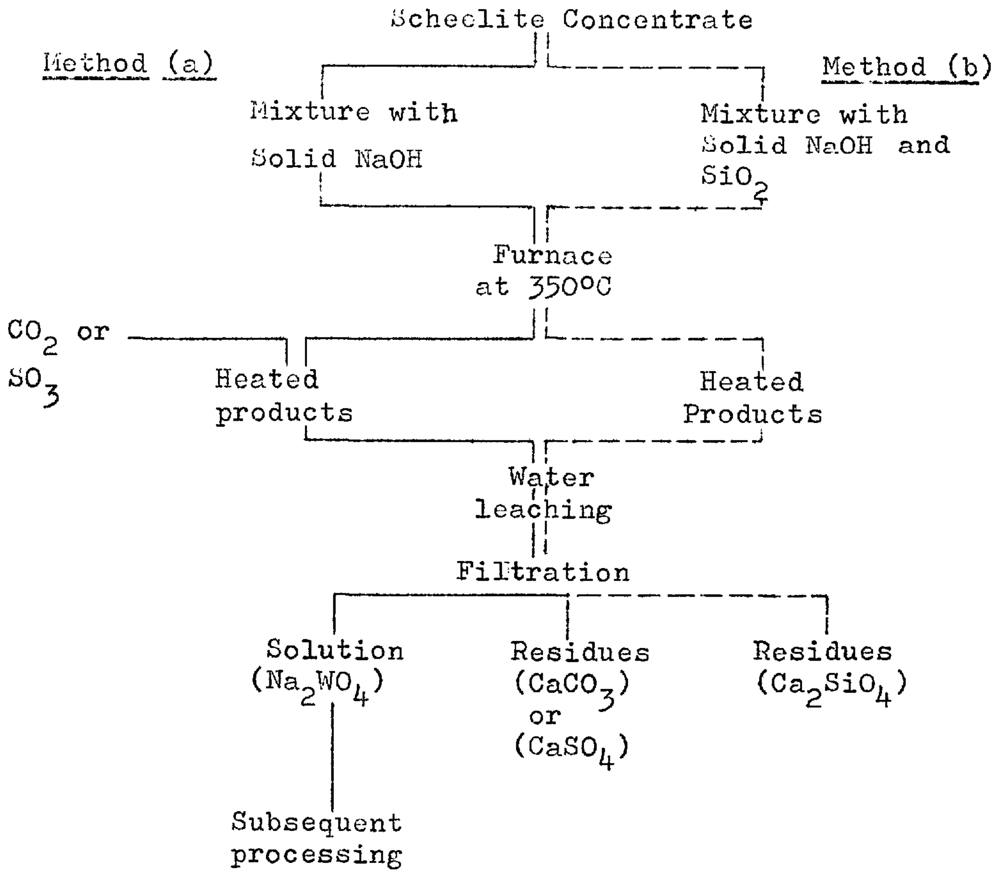

Fig. 51 A proposed flowsheet for processing of Scheelite with solid sodium hydroxide.

## 6. Some economic aspects of the fritting process.

As the fritting process offers technical advantages over the conventional alkali processes it is worthile trying to assess the possible economic advantages of the process.

Accurate assessment of the economy of the process is not easy because the relevant information is not readily available, but comparison with caustic leaching and fusion is possible and this will be attempted in the following section.

The principal differences between the normal industrial process and the fritting process which are relevant to the economics are listed in Tables 19 and 20, and in Table 21 the capital and running costs are compared. It can be seen that the major cost is the reagent, therefore the smaller reagent requirement for the fritting process is clearly the principal economic advantage. When the leaching and fusion processes are compared on this particular point alone, as follows:

The leaching process:
£60/ton of $NaOH^{*}$ x 1.5ton NaOH/ton of monazite
= £90/ton of monazite treated.

The fritting process:
£70/ton NaOH x 1.0 ton NaOH/ton of monazite
= £70/ton of monazite treated.

* Sodium hydroxide in the form of solution is cheaper than the solid.

The difference is £20 per ton of monazite treated. In other words the economy achieved by the fritting process would be approximately 20%.

Table 19. Comparison of the current industrial process with the fritting process.

Monazite Processing

| Principal items | Caustic solution process | Caustic fritting process | Economy (by the fritting process) |
|---|---|---|---|
| Equipment | Steam-heated reactor with agitator | Furnace | Slight reduction in capital and operational costs. |
| Particle size | Fine grinding required (-300 mesh) | as received | Economy in grinding cost. |
| Temperature | 140°C | 360°C | Little difference or slightly higher in fuel costs. |
| Time | 4 hr | 1hr | Economy in labour and maintenance cost. |
| wt. ratio $\frac{\text{NaOH}}{\text{mineral}}$ | 1.5 | 1.0 | 1/3 economy |
| Dissolution stage | agitated dilution only | dissolution with occasional stirring. | Little difference |

Table 20. Comparison of the current industrial process with the fritting process

Columbite Processing

| Principal items | Fusion process | Fritting process | Economy (by the fritting process) |
|---|---|---|---|
| Equipment | iron crucible, furnace | similar to fusion process | Little difference |
| Temperature | two step operation: 400°C → 800°C | 540°C | Slight reduction in fuel consumption. |
| Time | 1 hr | 1 hr | Little difference |
| Particle size | 100 mesh | 36 mesh | Economy in grinding cost. |
| weight ratio $\frac{\text{NaOH}}{\text{mineral}}$ | 3.0 | 1.2 | Reduction in reagent consumption |
| Dissolution in water | melt is poured into water | ready dissolution | Minor saving on safety precautions, etc. |

Table 21. Estimated costs on monazite processing(32)
(1ton/hr capacity for 5 year operation)

Principal equipment (ton/hr cap.)

| Fritting process | | Leaching by aqueous alkali | |
|---|---|---|---|
| Ore bin 50 ton cap. ... | £ 2000 | Ore bin ... ... | £ 2000 |
| Feeder ... ... ... | 500 | Feeder ... ... | 500 |
| Mixer, dry ... ... | 1000 | Grinding facilities | 2000 |
| Furnace, oil ... ... | 2000 | Reactor, stainless steel | 6000 |
| Agitator tank ... ... | 2000 | Agitator tank ... | 2000 |
| Auxiliary equipment ... | 1000 | Auxiliary equipment | 1000 |
| Building, maint., etc. | 4000 | Building, etc. ... | 4000 |
| Total | £12,000 | | £17,500 |
| | £2400/year | | £3500/year |
| Capital Cost per ton treated | 5/- | ... ... ... | 8/- |
| Labour Cost, 15/- x 3men | 45/- | ... 3 men ... | 45/- |
| Power, water etc. | 20/- | ... ... ... | 20/- |
| Reagent, NaOH 1ton at £70 | £70 | ... 1.5ton at £60 | £90 |
| | £73 - 10 - 0 | | £93 - 13 - 0 |

Advantage £94 - £74 = £20/ton treated *

(* This difference comes mainly from the reagent cost.)

When the fusion and fritting processes are compared on the same basis in the treatment of columbite, as follows;

The industrial fusion process for columbite:

£70 x 3.0 ton NaOH/ton of columbite

= £210/ton of columbite treated.

The fritting process for columbite:

£70 x 1.2 ton NaOH/ton columbite

= £84/ton of columbite treated.

In other words the cost by the fritting process may be as low as 40% of the cost of the conventional fusion process.

# PART IV

## SUMMARY

The reactivities of a number of minerals with solid sodium hydroxide have been investigated. The process, described as 'caustic fritting' is found to be useful for treating a number of economic minerals. The optimum processing conditions for monazite, wolframite, and columbite have been obtained. The summary of conclusion drawn from the investigation is as follows:

### The Reactivity of Minerals

1. The reagent, NaOH, not the mineral itself, has the dominant effect on the reactivity of many of the minerals.

2. The initial reaction of a number of minerals is probably associated with the phase changes of sodium hydroxide and the local liquifaction effect caused by the heat of reaction.

3. All the economic phosphate and tungstate minerals, as well as most of the siliceous gangue minerals are highly reactive at temperatures lower than the melting point of sodium hydroxide.

4. The iron oxide minerals and most of the iron bearing minerals are moderately inert to sodium hydroxide. Cassiterite is the most inert of the minerals found in beach sands.

5. Fine-grinding of the ore is un-necessary to achieve a satisfactory reaction rate when the mineral is processed by the fritting method; ordinary gravity separation products can be treated directly. Satisfactory decomposition is obtained by using less alkali and lower temperatures than the conventional fusion process.

6. The reaction products of fritting treatment are in the form of loose aggregates of small particles which can be leached

much more readily than a fused mass. The residual oxides after water-leaching are reactive to acids which facilitates subsequent processing.

7. For a good frit it is important to avoid heating to a temperature at which one or more of the product phases melt, and to employ the minimum ratio of sodium hydroxide.

8. Continuous operation is possible and the process could be readily integrated into existing plant.

9. Economic minerals which are readily amenable to this type of processing are monazite, xenotime, wolframite and columbite. Others which can be processed, though with some difficulty are scheelite, apatite, pyrochlore, chromite and ilmenite.

10. The results of the reactivity tests on many minerals suggest the possibility of processing by selective reaction of some pairs of minerals that are difficult to separate by physical methods, e.g. wolframite-cassiterite, xenotime (monazite) - zircon, columbite-cassiterite, apatite-iron oxide minerals.

11. The selective reaction test on a mixed wolframite-cassiterite concentrate has shown that the mixed values can be successfully separated by reacting wolframite and leaving cassiterite as unreacted solid, with recovery of more than 95% of tungsten and tin in the respective products.

The summary of the findings on monazite, wolframite, and columbite other than the above mentioned are as follows:

Monazite

1. There are two temperatures at which a marked increase in reactivity occurs. The Arrhenius equation is not obeyed in the low temperature range.

2. Of the product phases the rare earths and thorium oxides

formed a solid solution within which some of the sodium was also associated. The crystal structure of the new phase is cubic of sodium chloride type with a range of lattice constant $a_o = 5.57 - 5.49 Å$ depending on the various condition of heat-treatment and degree of leaching.

3. The sodium phosphate phase in the monazite reaction was found to be trisodium orthophosphate ($Na_3PO_4$), irrespective of the reaction temperature.

4. The chemical equations for the monazite reaction with sodium hydroxide have been formulated.

5. The excess sodium hydroxide required has been determined to be 20-30% of the stoichiometric requirement.

6. The optimum conditions of processing monazite are to heat an intimate mixture of monazite and ground sodium hydroxide (20 - 30% excess amount) to 350°C for an hour.

7. No significant difference is found with monazite from different origins, nor when the scale was increased from 10g. to 1kg.

## Wolframite

1. Satisfactory decomposition of a commercial grade of wolframite concentrate can be achieved by intimately mixing it with ground sodium hydroxide in a weight ratio, NaOH/concentrate = 1.2, and heating to 350°C.

2. The formation of sodium manganate can be prevented by reduction of the heating period to 30 minutes; the manganese is then left as insoluble oxide.

## Columbite

1. The optimum processing conditions of an unground commercial concentrate (36 - 150 mesh) are to heat the mixture of concentrate and sodium hydroxide in a weight ratio, NaOH/mineral = 1.2, to 540°C for an hour.

## Mixed Wolframite-cassiterite concentrate from South Crofty

1. The optimum processing conditions for the mixed concentrate are to heat an intimate mixture of the ore with ground sodium hydroxide in 1:1 weight ratio to 320°C for an hour.

2. Grinding or sizing of the ore is unnecessary.

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