

《Original》

Vitrification of Highly Active Liquid Waste (II)

(The thermal decomposition of HARVEST feed slurries and the characterization of the product)

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(July 13, 1979)

Abstract

The thermal decomposition of simulated Magnox highly active waste and of HARVEST feed slurries (SN and SG) which include the glass forming chemicals has been studied.

The waste and the slurries are almost completely calcined by 500-550°C. The colour of the solids from the slurries varies little until about 900°C when it darkens considerably. The slurries begin to vitrify at this temperature and are completely vitrified at 1000-1050°C. On the other hand, the sulphate impurity in SN slurry causes a yellow phase to separate above 750°C.

The density of the intermediate solids is fairly low until 650-700°C is reached. This temperature seems to mark the onset of fluxing as the density rises quickly to 2g/cm³ at 700-800°C. The strength of the solids decreases with temperature up to 500°C, and then rises as the solids begin to sinter. Below 500°C the SN solids are the stronger, suggesting that the impurity renders this silica more reactive.

요 약

Magnox 핵연료 재처리에서 발생되는 모의고준위 방사성폐액의 열분해와 이 폐액의 유리화를 위한 첨가제가 함유된 HARVEST 공급슬러리(SN과 SG)의 열분해에 관하여 연구되었다.

폐액과 슬러리는 500-550°C 범위에서 거의 완전히 가소 처리된다. 900°C 이하에서 슬러리로 부터 얻어지는 고화물들은 유사한 색채를 띄지만, 이 이상에서 대단히 짙은 색으로 변한다. 슬러리는 900°C에서 유리화하기 시작하여 1000-1050°C에서 완전히 유리화 된다. 한편, SN 슬러리내에 불순물로 존재하는 황화물은 750°C 이상에서 황색반점을 분리시키는 영향이 있다.

650-700°C 이하에서 얻어지는 고화물의 밀도는 대단히 낮고 700-800°C에서는 밀도가 2g/cm³로 급증됨으로서 650-700°C에서 용융되기 시작하는 것 같다. 500°C까지 온도가 상승함에 따라 고화물의 강도가 감소하고, 그 이상에서는 고화물의

소결현상으로 인하여 강도가 증가하게 된다. 500°C 이하의 SN 고화물은 SG 고화물에 비하여 강도가 훨씬 크고, 불순물로 존재하는 황화물은 silica 의 반응도를 높여 준다는 것을 암시하고 있다.

1. Introduction

A new inactive pilot plant has been built at Harwell for development work on the HARVEST process which is modification of the FINGAL concept^{1,2)} for the vitrification of highly active waste. The HARVEST process produces an alkali borosilicate glass from a slurry which is a mixture in 2M HNO₃ of (a) the waste mainly as nitrates and (b) the glass forming chemicals silica, lithium hydroxide or nitrate, sodium nitrate or carbonate, and sodium tetraborate. The temperature of the process vessel is maintained at about 1000°C, but the temperature of the various products within the vessel ranges from 120° to 1000°C whilst slurry is being fed. Evaporation, denitration and glass formation proceed simultaneously, and also physical changes occur in the solid phases as gas bubbles create porosity which later collapses when vitrification sets in.

The purpose of the present work was to analyse the decomposition of the feed mixture in terms of weight loss at various temperatures, and to make some simple measurements of the physical and mechanical properties of the solid phase at the various stages of decomposition.

2. Experimental

2.1 Material used

A simulated liqued waste based on Magnox fuel reprocessing, and complete feed slurries with added silica, alkali and borate were employed for the thermal decomposi-

tion studies. Two feed slurries were used. The first was made with Neosyl grade of silica (a precipitated form containing about 3.5% sulphate impurity). The other was made with Gasil WP grade of silica (a micronised silica gel). Chemical compositions of the waste itself and of the two feed

Table 1. Composition of Simulated Magnox Waste Expressed as Oxides

| Element | % Weight as Oxide |
|------------|-------------------|
| Ba | 1.77 |
| Cs | 4.15 |
| Mo | 6.59 |
| Rare Earth | 17.97 |
| Sr | 1.46 |
| Zr | 6.67 |
| U | 0.24 |
| Al | 20.10 |
| Cr | 2.20 |
| Fe | 10.80 |
| Mg | 24.94 |
| Ni | 1.39 |
| Zn | 1.72 |
| Total | 100.00 |
| Phosphate | 1.80 |

Table 2. Composition of Complete Feed Slurry Expressed as Oxides

| Oxides | % Weight | |
|-------------------------------|-----------|-----------|
| | Slurry SG | Slurry SB |
| B ₂ O ₃ | 11.1 | 11.1 |
| Li ₂ O | 4.0 | 3.5 |
| Na ₂ O | 8.3 | 7.3 |
| SiO ₂ | 50.9 | 52.6 |
| Waste | 25.7 | 25.5 |
| Total | 100.0 | 100.0 |

slurries expressed as oxides are given in Table 1 and 2, respectively. The concentrations of waste and feed slurry were 183g per litre and 300g per liter respectively expressed as oxides.

2.2 Decomposition

The waste and the feed slurries were thermally decomposed as follows: (1) Using a TGA Stanton thermobalance, they were heated up to 950°C at a constant heating rate of 3-4°C/min, in a slow air stream. (2) In addition other experiments were performed in which the slurries were heated in a separate furnace to various temperatures between 130° and 900°C, and then maintaining the temperature constant for 18 hours. The temperatures used are given in Table 3. The feed slurries were decomposed in 26-27mm diameter crucibles and yielded up to about a 10mm depth of product. The products obtained in this second series experiments were employed directly for the physical measurements without further treatment.

Table 3. Temperatures used in the Experiments

| Temperature (°C) |
|------------------|
| 130 |
| 150 |
| 200 |
| 250 |
| 300 |
| 400 |
| 500 |
| 600 |
| 650 |
| 700 |
| 750 |
| 800 |
| 900 |
| 1000 |
| 1050 |

2.3 Physical Measurement

Apparent bulk densities of the products, prepared by the thermal decomposition of feed slurries at various temperatures, were measured based on the bulk volume occupied in the crucible. An apparent modulus of the resulting solid was obtained by loading the solid in the crucible under compression with a 20mm diameter ram and measuring the load/extension curve with an Instron Testing Machine. A constant loading rate of 1-2mm/min and applied pressures of up to 73kg/cm² were used. In the early part of the test the slope of the load-extension curve gives an apparent elastic modulus of the solid, which in turn is an approximate measure of the strength of the solid. In the later part of the test after the porous solid had become completely broken up the slope of the curve now represents the consolidation behaviour of the resulting particulate mass.

3. Results and Discussion

3.1 Decomposition of Liquid Waste

The thermal decomposition curve of the simulated liquid waste is shown in Fig.1. The waste began to lose weight at 36°C continuing very slowly up to 80°C. From this point to about 200°C where an inflection appeared weight was rapidly lost. This is mainly evaporation of the free water and nitric acid in the waste but it also includes the decomposition of nitrate compounds which break down at comparatively low temperatures such as those of Aluminium, Chromium and Iron.³⁾ At 193°C the weight loss was 70.1% but after this point the rate of weight loss decreased.

From 300°C where the next inflection appeared the rate slightly increased to about 420°C at which temperature we expect the almost complete decomposition of nitrate

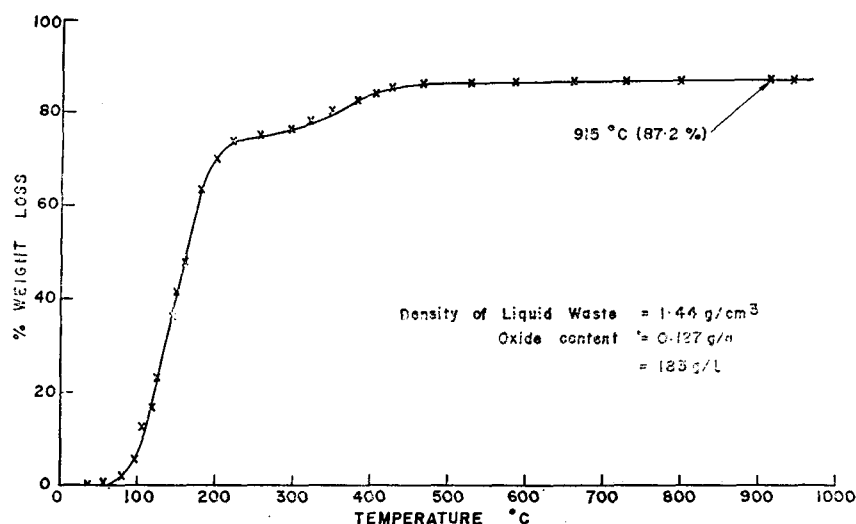


Fig.1. Thermobalance behaviour of simulated liquid waste

compounds except those decomposed at high temperature such as Barium, Caesium and Strontium.³⁾ At 420°C the weight loss was 85.5% and then more weight was lost very slowly to 526°C where a short horizontal appeared. The weight loss was 86.5% at 526°C. It is considered that at this temperature all the nitrate compounds except Barium, Caesium, Strontium, Rare Earth and Uranium have decomposed completely.

From 562°C the waste began to lose mass again very slowly up to 915°C at which a constant weight was reached. This is due to the completion of the decomposition of nitrate compounds remaining, as mentioned above. At 915°C the weight loss was 87.2%, virtually the same as the theoretical value (87.3%) corresponding to the complete conversion of the waste to oxides.

3.2 Decomposition of Feed Slurries

Slurries SN (using Neosyl silica) and SG (using Gasil WP silica) began to lose weight in the thermal balance experiments at about 40°C as shown in Fig.2 and 3. From 80° to 200°C weight was rapidly lost, due to the evaporation of free water and to the

decomposition of such nitrates as discussed above for the simulated waste alone. At 200°C the weight losses by thermobalance were 65.1 and 64.8%, respectively. After this point the loss rates decreased.

Decomposition continued smoothly to around 480°C and at this temperature the weight losses were 73.7% in slurry SN and 74.0% in slurry SG. From this point to 540°C at which their thermal decompositions were almost completed the loss rates slightly increased. At 540°C, the weight losses were 77.0 and 76.9% in slurry SN and SG respectively, i.e. within 1% of the calculated values for complete decomposition to oxides of 77.4 and 77.8% respectively.

It has been shown³⁾ that this temperature 540°C is not high enough to cause any significant decomposition of the individual nitrates of sodium and lithium. The contents of NaNO₃ and LiNO₃ in the slurries are about 4.8% and 3.9% respectively. When these are decomposed to oxides the corresponding weight loss of the slurry would be 3.1% due to each compound, i.e. a total weight loss of 6.2% (the individual

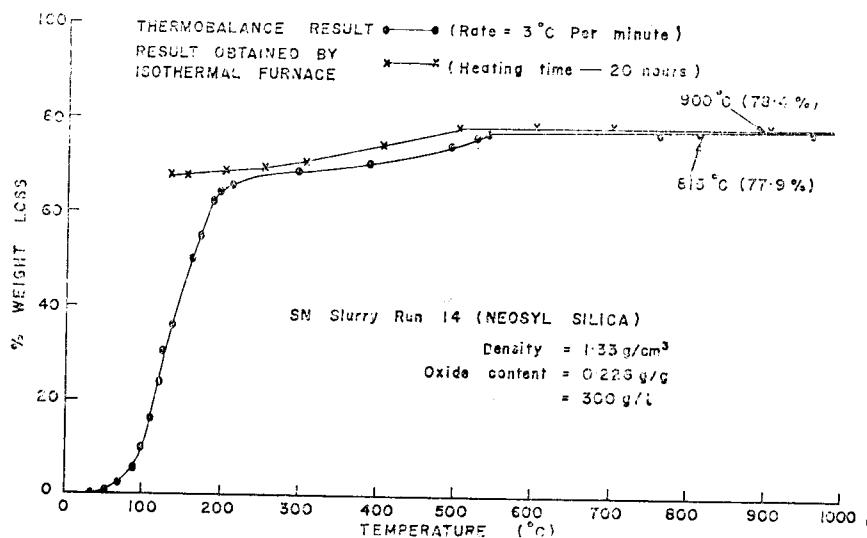


Fig.2. Decomposition of feed slurry SN

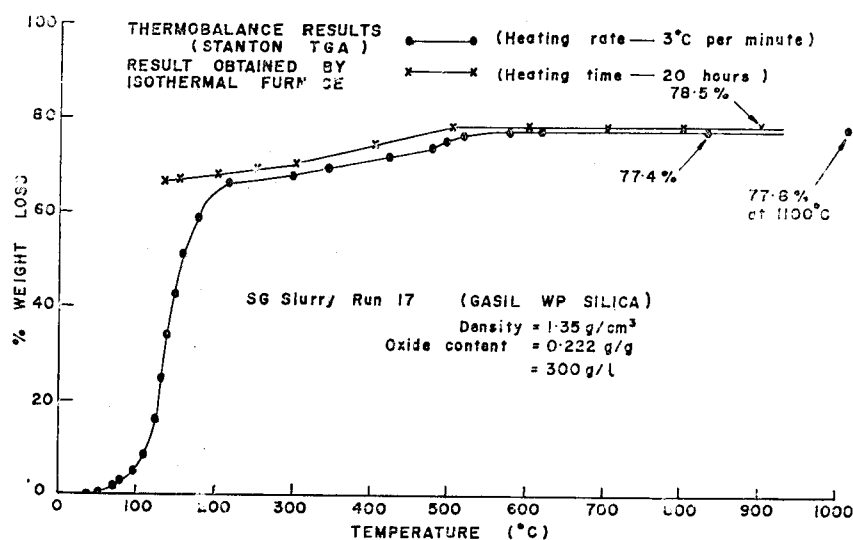


Fig.3. Decomposition of feed slurry SG

wieght losses are equal because the alkali metals are present in equal molar amounts). It is therefore clear that the decomposition of these two nitrates in the slurries must have already been almost completed by 540°C. The presence of other materials in the slurries (of which perhaps silica is the important species) is thus able to facilitate the decomposition of alkali nitrates at a

lower temperature than would otherwise be the case. Between 400°C and 650°C alkali nitrate could decompose as follows⁴¹:

- a. $2\text{NaNO}_3 + \text{SiO}_2 \rightarrow \text{Na}_2\text{SiO}_3 + 2\text{NO} + 3/2\text{O}_2$
- b. $2\text{NaNO}_3 + \text{Al}_2\text{O}_3 \rightarrow 2\text{NaAlO}_2 + 3/2\text{O}_2 + 2\text{NO}$
- c. $2\text{NaNO}_3 + \text{Fe}_2\text{O}_3 \rightarrow \text{Na}_2\text{Fe}_2\text{O}_4 + 2\text{NO} + 3/2\text{O}_2$

Constant weights were eventually reached on the thermobalance at 815°C for slurry SN and at 576°C for slurry SG and their

final weight losses were 77.9 and 77.4% respectively. When the slurries were heated in a separate furnace to steady temperatures for 18 hours, constant weights were reached earlier at 500°C but the weight losses were much the same at 78.4% in slurry SN and 78.5% in slurry SG. This indicates of course that the thermobalance is never in equilibrium, and it will always underestimate

the weight loss at any given temperature.

3.3 Bulk Density of Products

Variation of the apparent bulk densities of the products produced by thermal decomposition of the two slurries at various temperatures are illustrated in Figs. 4 and 5. The diagrams also show (a) the yield of total solids expressed as g per 100g of slurry, and (b) the bulk density of the

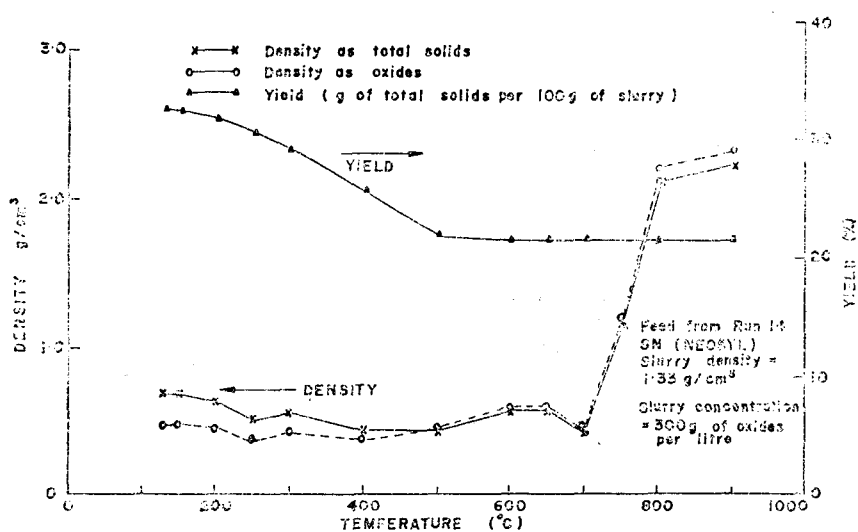


Fig.4. Density and yield of solids from slurry SN as a function of temperature

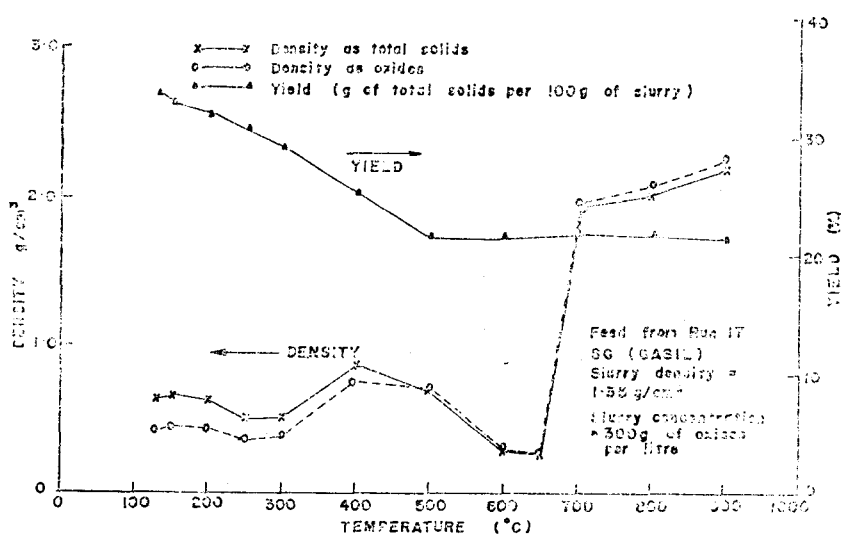


Fig.5. Density and yield of solids from slurry SG as a function of temperature

solid in terms oxides. The latter curve indicates directly how the bulk volume changes - a low oxide density corresponds to a high volume, and vice versa. Between 130°C and 150°C the densities of the products slightly increased and then decreased up to 250°C. At this temperature the densities of SN and SG solids were 0.52 and 0.51g/cm³ respectively.

The initial increase is due to compacting as free water evaporates and the decrease is due to the formation of nitrous gas bubbles as the nitrate compounds begin to decompose.

At 400°C the density of SN was 0.45g/cm³ while that of SG was much higher at 0.86 g/cm³. Between 400°C and 650°C the density of SN product slightly increased, while that of SG product decreased considerably. At 650°C the densities of SN and SG solids were 0.58 and 0.25g/cm³, i.e. the order was reversed.

The lowest densities of 0.45 and 0.25 appeared at 700°C for SN and at 650°C for SG respectively. These minima are due to

the formation of a foam bridge across the crucible which enclosed substantial voids probably created by residual gases escaping as the solid started to flux. Above these temperatures the densities rapidly increased, due to the progress of sintering as the glassy state is approached. At 900°C the densities of SN and SG were 2.23 and 2.20g/cm³, which may be compared with the density of the fully vitrified product at 1000°C of 2.60g/cm³.

3.4 Appearance of the Decomposition Products

The appearance of the samples of both slurries heated up to 300°C was almost the same as shown in Figs. 6 and 7, except that the colours changed at 250°C corresponding to the appearance of the lower apparent density. SN products formed a coherent mass up to 600°C compared with SG products which were very soft and fine and less bulky up to 500°C. This suggests that up to 500°C Neosyl silica has a stronger chemical interaction than Gasil, perhaps due to the sulphate impurity.

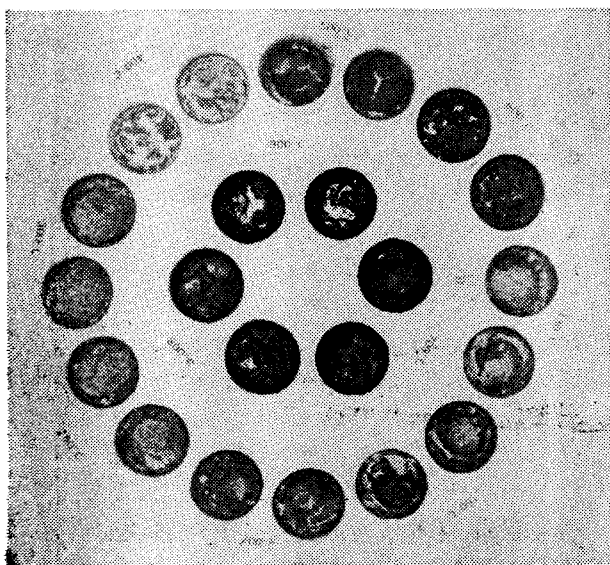


Fig.6. Appearance of products from slurry SN

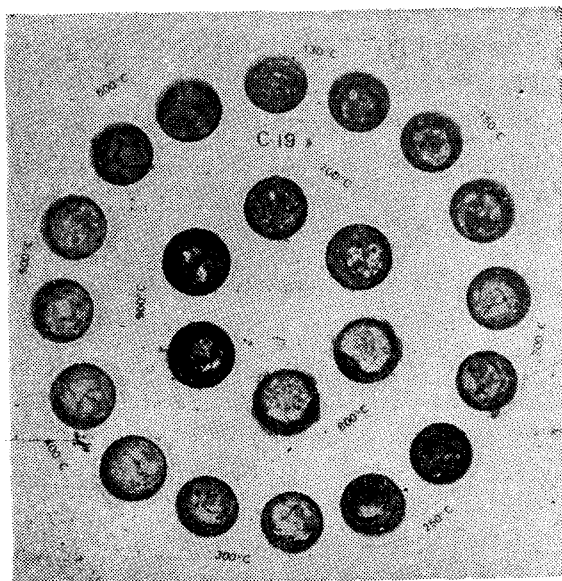


Fig.7. Appearance of products from slurry SG

As shown in Fig.7 with SG feed a bridge of material was formed across the crucible at 600°C following a large expansion. The bridge was still present at 650°C. This bridge formed with SN feed at 700°C(Fig.6) following a smaller expansion. At higher temperatures collapse as most of the chemicals flux and slowly melt down along the crucible wall.

At 800°C the colour of SG was the same as SN, except that the latter has yellow spots. Based on the above it could be concluded that the sintering point of the SN system is higher than the SG mixture; the difference is in the region of 50°-100°C. This is to be expected in view of the lower alkali content in feed SN, see Table 2.

Some yellow spots began to appear in SN material at 750°C and these are visible from 800°C in Fig.6. These spots had a tendency to grow at elevated temperatures. This phase originates because of sulphate which is present in the Neosyl as an impurity¹⁾, and it also contains molybdate and chromate³⁾.

At 900°C the general colour became darker, due to the onset of vitrification. A green phase, which was formed at 800°C, remained in the crucible even when heated up to 900°C. But at 1000°C, the colour changed, and represents the completion of vitrification.

3.5 Mechanical properties

The simple stress/strain tests carried out on the solids as produced in the crucible give an indication of the mechanical properties of the porous solids which are formed before the temperature is high enough for vitrification. The load/extension curve was initially linear and so is a measure of an effective elastic modulus. Since the fracture strain of many ceramic materials is approx-

imately constant we can take this initial slope to be also a measure of the strength of the solid. Thus the observed relationship is;

$$S = N_1 \epsilon$$

At high loads when the solid has been crushed to a powder the load/extension curve is exponential in nature as follows:

$$\text{Log } S = N_2 \epsilon + K$$

where S is the applied stress (kg/cm²), ϵ is the strain measured from the beginning of the compressive test (dimensionless), and N_1 and N_2 are slopes in the initial and final stages respectively and K is a constant. N_1 has the dimensions of stress, but N_2 is dimensionless. The strain in the first stage ranged from zero up to 0.03-0.15 for SN and up to 0.05-0.28 for SG, and in the final stage between 0.30 and 0.40 for SN and between 0.40 and 0.82 for SG.

The parameters N_1 and N_2 are illustrated in Figs. 8 and 9 as a function of the treatment temperature. Figure 8 shows that the trends of the variation of N_1 with temperature are similar for both feed slurries and that N_1 is greater for SN except for the products prepared at 600°C. These results suggest that the intermediate products formed during the vitrification of the SN feed are stronger than SG products (except at 600°C). Visual observation confirmed that a more coherent mass is formed from SN feed as mentioned in section 3.4.

At 150°C the values for N_1 are relatively high, due to the densification achieved by the evaporation of free water of crystallisation as described in section 3.3. N_1 (hence the strength) then decreased as the temperature rose to 500°C. This is presumably due to the gas evolution created by the decomposition of nitrates.

As shown in Fig. 8, the strength of the

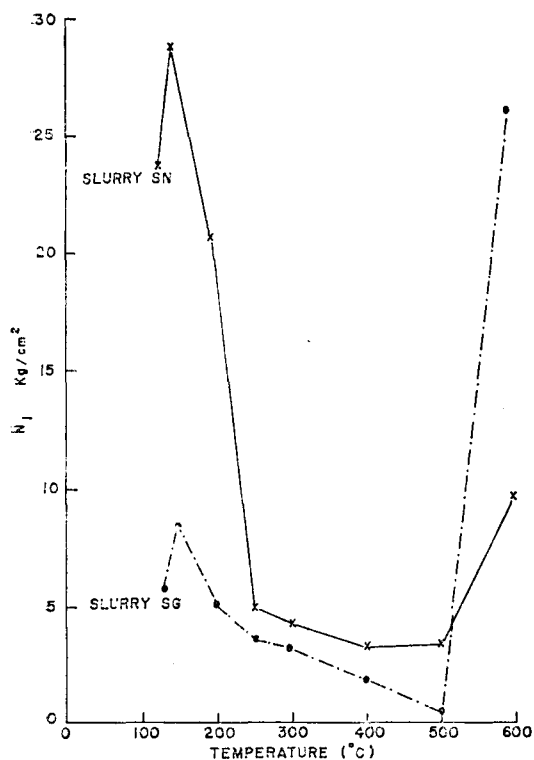


Fig. 8. Apparent modulus of solids as a function of decomposition temperature

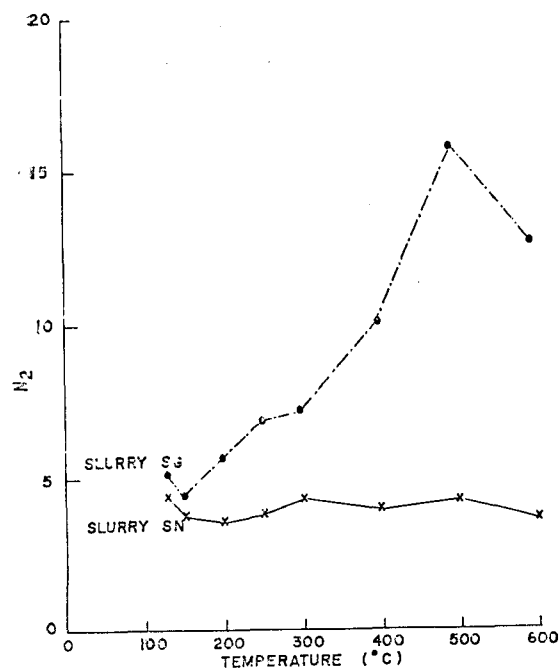


Fig. 9. Consolidation index of crushed solids as a function of decomposition temperature

products from SN and SG increased for temperatures beyond 500°C. Thus we see that the solids are weakest in the temperature range 250–500°C which is the range of decomposition temperature for most of the nitrates. The solid is stronger at low temperature because not much porosity has been formed, and is stronger at high temperature because sintering is then beginning as a prelude to glass formation.

The parameter N_2 for the SN powder was approximately constant independent of temperature (Fig. 9) but for SG powder N_2 increased with temperature up to 500°C. The results imply that powders obtained after crushing the various products are more difficult to consolidate when based on Gasil WP silica than Neosyl silica. The explanation of this difference appears to be related to the fact that the crushing of the SG products yields a bulk material with fewer voids and so it resists consolidation more. The SN products when crushed, perhaps because of their initial greater strength (see Figure 8), presumably yield a less favourable range of particle sizes and so contain more voids. At a given applied load they will therefore offer less resistance to consolidation.

4. Conclusions

The temperature at which the slurry feed completely decomposes is lower than that of some individual nitrates. This suggests that the decomposition temperature of the nitrates is decreased by the presence of the glass formers, of which the silica is probably the most important.

The bulk density of the intermediate products yielded by the slurry feeds is low in the temperature range up to 500°C which

is the point at which virtually all decomposition has been completed. The density of SN products ($0.4\text{--}0.6\text{g/cm}^3$) is lower than that of SG products ($0.5\text{--}0.8\text{g/cm}^3$). Over this same temperature range the SN products are stronger and more coherent. This suggests that the Neosyl silica, perhaps because of its sulphat impurity, interacts with the decomposing nitrates to form a stronger structure which does not therefore collapse so readily.

Between 500°C and 700°C the relatively strong SN solids show little further volume change. However the SG solids show a marked expansion at 600°C accompanied by a substantial gain in strength. Presumably fluxing has just commenced and residual gases expand the structure which does not now collapse, a process which had occurred at a lower temperature with the more reactive SN material. Sintering and rapid densification then follow in both cases, with SG and SN reaching 2g/cm^3 at 700°C and 800°C respectively.

The slurries begin to vitrify at about 900°C and are completely vitrified at $1000^\circ\text{--}1050^\circ\text{C}$. When using slurry based on Neosyl, containing the sulphate impurity, yellow spots of a separate phase begin to appear

at about 750°C and then grow at elevated temperatures.

When the intermediate decomposition products are mechanically broken up, the SG system yields a fine powder of relatively high bulk density, whereas the stronger SN system yields particles which pack less tightly. The latter is consequently more compliant to the application of further mechanical loading.

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