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MASTER

NEW YTTRIA PLASTERS

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January 1978

**UNION
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OAK RIDGE Y-12 PLANT
OAK RIDGE, TENNESSEE

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NEW YTTRIA PLASTERS

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ABSTRACT

The physical and chemical properties of a new, sinterable yttria (Y_2O_3) plaster, formed in the yttria/acid/water (dilute-acids) system, were determined. The binder phases responsible for plaster formation were of the form $\text{Y}_2(\text{OH})_{6-m}\text{X}_m \cdot n\text{H}_2\text{O}$, with $m = n \sim 1$ and X represents either Cl^- or NO_3^- . Binder-phase decomposition behavior was studied by thermal analysis.

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SUMMARY

A new, sinterable yttria (Y_2O_3) plaster was developed. The properties of this plaster depend on: (1) starting-powder characteristics, (2) type and concentration of the acid used for the liquid phase, and (3) the liquid-to-powder (L/P) ratios. Physical and chemical properties of the yttria plaster were investigated.

Plasters formed in the yttria/acid/water (dilute-acids) system were determined to consist mostly of needle (or plate)-shaped hydroxysalt binder phases analogous to precipitates in the YX_3 /sodium hydroxide/water system (where X represents either Cl^- or NO_3^-). The binder phases were shown to be of the form $Y_2(OH)_{6-m}X_m \cdot nH_2O$, where m and n generally equal one.

The decomposition behavior on heating yttria plasters was studied by thermal analyses. The nitric acid-produced plasters decomposed to yttria below $600^\circ C$ in argon; the hydrochloric acid-produced plasters decomposed to yttria by $1520^\circ C$ in argon or by $1100^\circ C$ in air.

Examination of scandium oxide and the rare-earth oxides showed that several exhibited a plaster-forming behavior similar to yttria.

INTRODUCTION

While investigating the use of yttria coatings for the graphite crucibles used in uranium melting operations at the Oak Ridge Y-12 Plant,^(a) dilute nitric acid solutions were used with yttria powder in an attempt to form a stable suspension that was free of any carbon-containing suspension agent. A material resembling plaster of paris resulted. Because of the potential use of yttria cementitious phases with reactive materials (such as lithium, lithium hydride, nickel, titanium, zirconium, and uranium) with which yttria is thermodynamically stable, this investigation was undertaken. The first part of the study was directed toward yttria plaster, a rapidly formed, porous material useable for coatings, molds, microfilters, and castable thermal and electrical insulators.

Although there is considerable information in the literature on the mechanism and kinetics of formation of calcium sulfate hemihydrate plasters (ie, by Schiller,¹ Taplin,² Ridge and Surkevicius,³ Ridge and King,⁴ Jacobs,⁵ and Lambe and Ofutt⁶), there is apparently no report of any other analogous hydration system yielding a plaster. The recent binder classification scheme proposed by Sychev^{7,8} considers gypsum plaster, and portland and calcium aluminate cements as hydration materials where crystallization of a sparingly soluble or insoluble compound (new phase) results from a supersaturated solution. Considering this broad class of binder (chemical interaction to form a new phase), a subgroup consists of cements formed from an acid/base interaction, such as the phosphate cements studied by Kingery^{9,10} and a wide variety of acid/oxide reaction cements reported by Federov.¹¹ The plaster prepared from yttria and dilute acids appears to be a new hydration product that has a closer association to gypsum plaster than to cements ordinarily formed from an acid/oxide reaction.

(a) Operated by the Union Carbide Corporation's Nuclear Division for the Department of Energy.

NEW YTTRIA PLASTERS

EXPERIMENTAL PROCEDURE

Preparation of the Plaster

A plaster of yttria was produced by: (1) mixing yttria powder^(b) (nominally > 99.9 wt % pure) with a dilute acid solution and stirring until a fluid slurry or suspension resulted; (2) casting the slurry into a mold or around a mandrel (eg, fluorocarbon-coated metal or glass); and (3) allowing for an incubation period wherein the material "sets" [about 5 to 30 minutes, depending primarily on the particle size, acid concentration, and liquid-to-powder (L/P) ratio].^(c) The setting was exothermic. After setting, the as-formed plaster was thoroughly dried in air from 20 to 60°C before examination.

The yttria plaster was prepared from a starting powder with mean particle diameters ranging from 0.05 to 25 μm . The optimum material had agglomerates,^(d) with a mean overall diameter of 3.5 μm , consisting of particles with a mean diameter of 0.06 μm .^(e) In general, larger particle sizes resulted in a faster setting time, but the plaster had less strength.

Nitric and hydrochloric acid solutions allowed rapid (5 to 30 minute) formation of a coherent plaster. Other acid solutions (ie, HF, HBr, HI, HClO₄, HCOOH, CH₃COOH, H₂SO₄, H₃PO₄, and H₂CO₃) caused a slower setting time, a weaker plaster, or no evidence of hydration bonding (as in H₂CO₃).

Nitric acid concentrations from 0.61 to 3.95 M were used, with 1.44 to 3.16 M being preferred for rapid plaster formation. Concentrations greater than 3.16 M were unmanageable, causing instant and nonuniform hardening before mixing could be completed; whereas, concentrations less than 1.44 M required long times (greater than one hour) to cause hardening of the plaster. For hydrochloric acid solutions, concentrations of 1.34 to 2.42 M were used to prepare the plasters.

Liquid-to-powder ratios from 0.56 to 1.44 were used, with the lower value being limited by the requirement of having a workable mix. When the L/P ratio exceeds 1.44, plaster will form under the excess liquid. The lower L/P ratios cause shorter setting times (ie, 2 - 5 minutes). An L/P ratio of 1.0 was generally used.

An examination was made of the effects on plaster formation of adding different materials to yttria. The reactivity of yttria plaster was also investigated, as was its sinterability. A

(b) A product of the Michigan Chemical Corporation, St. Louis, Michigan.

(c) L/P represents the ratio of the liquid (dilute acid) volume in milliliters to the powder weight in grams.

(d) Agglomerate size by Micromerograph.

(e) Particle size by electron microscope.

flowing argon (~ 30 l/min) atmosphere was used in a resistance-heated graphite furnace (ASTRO Model 1000A) with a platinum sample support. Temperature was controlled with a Research, Inc Data Trak card programmer using a Pt/Pt-10 Rh thermocouple.

Because of the general chemical similarity of yttrium with scandium and the rare earths, attempts were made to form plasters with each of their oxides (nominally $> 99.9\%$ pure), excluding promethium, using nitric or hydrochloric acid in the same manner as with the yttria plaster.

Preparation of Yttrium Hydroxynitrate and Hydroxychloride Hydrates

For comparison with yttria plasters [from the Y_2O_3/HNO_3 (or HCl)/ H_2O system], precipitates in the $Y(NO_3)_3/NaOH/H_2O$ and $YCl_3/NaOH/H_2O$ systems were produced. The hydrated salts [$Y(NO_3)_3 \cdot nH_2O$ and $YCl_3 \cdot nH_2O$ (where $n \approx 6$)] were prepared by completely dissolving yttria in concentrated nitric (7.9 M) or hydrochloric (6.0 M) acid solutions, followed by evaporation to dryness. To a dilute solution of the yttrium salt, a dilute solution of sodium hydroxide was added with the OH^- -to- Y^{+3} ratio ranging from 1 to 2. The precipitate was heated to $60^\circ C$ for 15 minutes while stirring before being washed and filtered to remove sodium salt. The precipitate was then dried at $60^\circ C$ for 24 hours and examined.

Chemical and Phase Analyses

The nitric and hydrochloric acid-produced plasters, along with the precipitated hydroxysalt phases, were analyzed for yttrium (X-ray fluorescence, $\pm 0.01\%$ ^(f)); oxygen (neutron activation, $\pm 0.1\%$), and hydrogen, nitrogen, and chlorine (standard chemical analyses, $\pm 0.2\%$). Dual aliquots were taken. Densities of the precipitated phases were measured by toluene displacement.

Each of these materials was examined by X-ray diffraction (XRD) techniques, using a 114.6-mm Debye-Scherrer camera with nickel-filtered $Cu K\alpha$ radiation. In addition, samples were step scanned, using a Siemens diffractometer equipped with a graphite monochromator and scintillation detector combined with a single-channel pulse height analyzer. A $1/2$ -degree entrance aperture slit was used so that the sample would intercept the entire beam ($Cu K\alpha$ radiation) at low 2θ values.

For yttria plasters (HNO_3 and HCl produced), a quantitative phase analysis of yttria was carried out by diffractometry, using the internal-standard technique.^{12,13} Linde A corundum (Al_2O_3) was used as the internal standard. The standard curve was determined by measuring the intensity ratio of the (400) yttria peak to the (012) alumina peak of a 1-to-1 (by weight) mixture of yttria and alumina. The intensity ratio for this mixture was 3.18 ± 0.04 (95% confidence interval, as determined by repetitive runs).

(f) Typical standard deviation from reported values.

Physical Characterization

Each of the plasters formed was examined by scanning electron microscopy to determine their morphology. The nitric and hydrochloric acid-produced yttria plasters were examined by standard mercury intrusion porosimeter techniques (as given by Drake and Ritter¹⁴)(g)

Hardness of the nitric acid-produced yttria plaster (L/P = 0.56, using 2.63 M HNO₃) and technical-grade plaster of paris [water-to-powder ratio (W/P) = 0.7] casts was determined using the Rockwell Y (1.27-cm-diameter) ball penetrator with a 15-kg load. The average of 14 measurements is reported with the standard deviation.

Thermal Analyses

Simultaneous differential-thermal-analysis (DTA)/thermal-gravimetric-analysis (TGA)^(h) data were undertaken for both the nitric and hydrochloric acid-produced plasters and for the precipitated hydroxysalt phases. These studies were in a flowing (4 to 6 l/h) argon or air atmosphere with alumina as the reference material and a platinum crucible. Temperature was measured with a Pt/Pt-10 Rh thermocouple, and a 6° C/min heating rate was used.

Complementing the DTA/TGA studies, thermogravimetric quadrupole mass spectrographic (TG-quad) analyses were conducted [vacuum $< 10^{-4}$ torr ($< 1.33 \times 10^{-2}$ Pa)] for the plasters in order to determine the evolved gaseous species.

RESULTS AND DISCUSSION

Properties of Yttria Plaster

The plasters produced by the procedure just described have⁽ⁱ⁾ porosities in the range of 50 to 65%, average pore diameters of 0.5 to 2 μm , bulk densities of 1.1 to 1.6 g/cm³, and apparent specific gravities of 2.7 to 3.3. Essentially all of the plasters had pore diameters less than 10 μm .

Examination of yttria plaster by the scanning electron microscope (SEM) revealed that the material is a mass of tangled needle and plate-like crystals having random orientation, yielding a continuously connected network of small pores. These features are seen in Figure 1 for nitric acid-produced plaster (where some unreacted yttria powder is visible),

(g) Described completely in *Aminco Digital Readout Porosimeter*, Catalog 5-7121A, Instruction 907-C, published by the American Instrument Co, Inc, February 1968.

(h) Thermoanalyzer Model TA1, Mettler Equipment Corporation, Princeton, NJ.

(i) Data from porosimetry.

Figure 1. A3-FORMED YTTRIA PLASTER. (L/P = 1.44, Using 3.16 M HNO_3 ; All Figure Widths of Photomicrographs Represent $\sim 11 \mu\text{m}$)

resembling a matrix of cotton. The hydrochloric acid-produced plaster has an appearance that is similar to the nitric acid-produced material except that the needles (or plates) are smaller for the former ($0.2 - 0.5 \mu\text{m L} \times \sim 0.05 \mu\text{m W}$) than for the latter ($0.2 - 1.0 \mu\text{m L} \times 0.05 - 0.1 \mu\text{m W}$).

Because the appearance of yttria plaster is equivalent to plaster of paris, a comparison between the Rockwell hardness number (RHN) values of nitric acid-produced yttria plaster and plaster of paris with similar porosities (50% for the former and 53% for the latter) was undertaken to further point out their similarities. The yttria plaster had a RHN value of 103 ± 5 and the gypsum plaster a value of 82 ± 5 . The hardness difference (25%) is related to the bonding that takes place between the plaster needles and to the needle size. (Note that, from SEM observation, the needles of nitric acid-produced yttria plaster are about a tenth the size of the gypsum needles.)

Initial XRD analysis of yttria plaster produced from dilute nitric acid or hydrochloric acid showed the presence of yttria (as the major phase) along with an unidentified(j) phase. A review of the literature on hydroxysalts revealed that yttrium "basic" salts of approximate formula $\text{Y}_2(\text{OH})_5\text{X} \cdot n\text{H}_2\text{O}$ (where $\text{X} = \text{NO}_3^-$ or Cl^- and $n = 1 - 2$) are precipitated from Y salt/alkali hydroxide/water systems^{15 - 19} and that, generally, dehydrated phases of the same stoichiometry result from hydrothermal ($\sim 400^\circ\text{C}$, $\sim 1200 \text{ atm}$) conditions.^{20 - 22} The XRD data available²³ for the hydrothermally prepared phases (one of which corresponded with the formula just given) did not match the diffraction patterns from the yttria plasters. Samples were prepared, since the precipitates were the only reported nitrate and chloride hydroxysalts for which XRD data were not available. The XRD observed patterns of the precipitates account for the unidentified XRD patterns in the plasters.

Table 1 lists the results of the analyses of the yttria plaster and precipitated phases. It is apparent that the hydration binder phase is of the general form $\text{Y}_2(\text{OH})_{6-m}\text{X}_m \cdot n\text{H}_2\text{O}$ (where $m \approx 1$ and $n \approx 1$ for the HNO_3^- produced plaster and for the precipitated phase). A cyclic formation technique (acid reaction, drying, and grinding for each cycle) was attempted with both nitric acid and hydrochloric acid to eliminate free yttria; the former resulted in the appearance of unidentified XRD lines in addition to the normal-binder-phase XRD pattern (after 5 cycles with 1.76 M HNO_3 , $\text{L/P} = 1.0$), although the latter caused no change in the XRD pattern of the hydroxychloride binder phase (after 5 cycles with 1.34 M HCl , $\text{L/P} = 1.0$). The hydroxychloride binder thus appears to have a wider homogeneity range than does the hydroxynitrate binder. Chemical analysis of the hydroxychloride binder from cyclic formation revealed essentially $\text{Y}(\text{OH})_2\text{Cl}$, (see Table 1) which has been previously reported.^{24 - 26} However, the XRD patterns of the chloride-containing materials listed in Table 1 were the same. It appears that $0.75 \leq m \leq 2.0$ and $0 \leq n \leq 1$ represent the

(j) From data available in the Powder Diffraction File, Joint Committee on Powder Diffraction Standards, 1601 Park Lane, Swarthmore, PA 19081.

Table 1
ANALYSES OF YTTRIUM HYDROXYNITRATE AND HYDROXYCHLORIDE PHASES

	System					
	Y ₂ O ₃ -HNO ₃ -H ₂ O ⁽¹⁾	Y ₂ O ₃ -HCl-H ₂ O ⁽²⁾	Y ₂ O ₃ -HCl-H ₂ O ⁽³⁾	Y(NO ₃) ₃ -NaOH-H ₂ O ^(4,6)	Y(NC ₃) ₃ -NaOH-H ₂ O ^(5,6)	YCl ₃ -NaOH-H ₂ O ^(5,6)
Y ₂ O ₃ (wt %) ⁽⁷⁾	24.6 (± 0.6)	30.0 (± 1.4)	0	-	-	-
Binder Phase (wt %) ⁽⁸⁾						
Y ³⁺	34.79	41.18	47.39	51.07	50.85	53.46
Cl ⁻	-	5.85	19.33	-	-	12.08
NO ₃ ⁻	12.62	-	-	16.64	15.23	-
OH ⁻	16.49	20.83	33.62	24.74	25.01	24.89
H ₂ O ⁽⁹⁾						
Remaining H ₂	3.40	5.89	0.48	4.95	8.04	7.69
Remaining O ₂	12.52	2.09	0	7.88	9.03	9.81
Total Difference	11.50	2.14	0	7.55	8.91	9.57
Y ³⁺ :OH ⁻ :X ⁻ (mole fraction)	1:2.48:0.52	1:2.64:0.36	1:1.98:1.02	1:2.53:0.47	1:2.57:0.43	1:2.43:0.57
H ₂ O (mole fraction) ⁽⁹⁾						
Remaining H ₂	0.19	0.82	0.03	0.27	0.45	0.43
Remaining O ₂	0.69	0.25	0	0.44	0.50	0.54
Total Difference	0.64	0.26	0	0.42	0.49	0.53
Binder Phase Formula	Y(OH) _{2.48} (NO ₃) _{0.52} · 0.19 - 0.69 H ₂ O	Y(OH) _{2.64} Cl _{0.36} · 0.25 - 0.82 H ₂ O	Y(OH) _{1.98} Cl _{1.02} · 0.0 - 0.03 H ₂ O	Y(OH) _{2.53} (NO ₃) _{0.47} · 0.27 - 0.44 H ₂ O	Y(OH) _{2.57} (NO ₃) _{0.43} · 0.45 - 0.5 H ₂ O	Y(OH) _{2.43} Cl _{0.57} · 0.43 - 0.54 H ₂ O
Density ⁽¹⁰⁾ (g/cm ³)	-	-	2.43	2.83	2.80	2.75

(1) Plaster: Prepared with 3.16 M HNO₃; L/P = 1.0.

(2) Plaster: Prepared with 2.42 M HCl; L/P = 1.0.

(3) Plaster: Prepared with 1.34 M HCl; reacted, dried, and ground 5 cycles; L/P = 1.0, each cycle.

(4) Precipitate: Ratio (OH⁻:Y³⁺) = 1.0.

(5) Precipitate: Ratio (OH⁻:Y³⁺) = 2.0.

(6) Precipitate: Hydroxide solution added to nitrate solution.

(7) Determined by XRD quantitative phase analyses; 95% confidence interval is given in parentheses.

(8) Elemental analyses were adjusted to the formula Y(Cr)_{3-m}X_m·nH₂O, where X represents Cl⁻ or NO₃⁻.

(9) Calculated from remaining hydrogen, remaining oxygen, or from the total difference necessary for 100% when summing constituents.

(10) Determined by toluene displacement.

range over which the hydroxychloride binder phase may retain the same crystal structure. It should be also noted that drying these materials (20 to 60° C) appears to cause no distinct changes in their XRD patterns.

The XRD patterns of the precipitated hydroxysalt binder phases are reported in Tables 2 (nitrate) and 3 (chloride). These XRD patterns are suitable for identification of these phases in yttria plasters. For the nitric acid and hydrochloric acid-produced plasters in Table 1 (single cycle), the presence of a large amount of yttria (as previously noted) was indicated. Ratio of the heights of

Table 3
X-RAY DIFFRACTION PATTERN OF
 $Y_2(OH)_{4.86}Cl_{1.14} \cdot 1.07 H_2O$
BINDER PHASE

d-Spacings ⁽¹⁾ (Å)	I/I ₁₀₀ ⁽²⁾	d-Spacings (Å)	I/I ₁₀₀ ⁽²⁾
8.46	100	1.888	2
7.00	1	1.859	3
5.00	6	1.819	9
4.23	15	1.784	8
4.00	3	1.749	4
3.77	5	1.670	5
3.56	2	1.621	< 1
3.49	4	1.582	2
3.33	3	1.556	4
3.16	/	1.531	4
3.10	28	1.479	3
2.96	12	1.461	1
2.92	14	1.421	< 1
2.81	1	1.371	2
2.75	< 1	1.296	1
2.59	3	1.262	< 1
2.50	8	1.236	< 1
2.33	6	1.220	< 1
2.29	6	1.187	2
2.23	5	1.174	1
2.17	5	1.160	1
2.08	4	1.141	< 1
2.05	3	1.128	< 1
2.03	4	1.112	1
2.01	6		

(1) Precipitated by the addition of NaOH to a YCl_3 solution (ratio of $OH^-:Y^{+3} = 2.0$); formula based on chemical analysis, with the water content representing the average calculated from remaining oxygen or by difference (see Table 1).

(2) Peak height intensities, diffractometer, Cu $K\alpha$ radiation.

Table 2
X-RAY DIFFRACTION PATTERN OF
 $Y_2(OH)_{5.14}(NO_3)_{0.86} \cdot 0.99 H_2O$
BINDER PHASE

d-Spacings ⁽¹⁾ (Å)	I/I ₁₀₀ ⁽²⁾
9.22	100
4.60	32
3.19	5
3.12	20
2.53	< 1
2.40	< 1
2.23	< 1
2.04	< 1
1.824	3
1.781	3
1.590	1
1.553	2
1.252	< 1
1.166	< 1

(1) Compound was precipitated by the addition of NaOH to a $Y(NO_3)_3$ solution (ratio of $OH^-:Y^{+3} = 2.0$); formula based on chemical analysis, with the water content representing the average calculated from remaining oxygen or by difference (see Table 1).

(2) Peak height intensities, diffractometer, Cu $K\alpha$ radiation.

the most intense peaks (9.22 Å peak of hydroxynitrate to 3.07 Å peak of yttria) is 0.36 for a plaster which contained only 24.6 wt % yttria. Similarly, for the hydrochloric acid-produced plaster, the ratio (8.46 Å peak of hydroxychloride to 3.07 Å peak of yttria) is 0.37 for a plaster which contained 30.0 wt % yttria. These observations are indicative of the much lower diffracting power of these hydroxysalts compared to yttria. This difference might be expected since the hydroxysalt binder phases contain a high percentage of low-atomic-number atoms and have relatively low densities.

Similarity of the XRD patterns of the hydroxysalt phases can be seen in Figure 2.

Figure 2. X-RAY DIFFRACTION SCANS FOR TWO YTTRIUM BINDERS.

The close correspondence of the formulae and XRD patterns of the hydrated hydroxynitrate and hydroxychloride binder phases is in accord with the observation of other workers^{21,22} for phases of similar composition (except dehydrated). The crystal structures of the hydrated hydroxynitrate and hydroxychloride binder phases are probably closely related. Attempts at indexing the XRD patterns or growing single crystals have been unsuccessful.

Thermal analyses of yttria plasters and precipitated hydroxysalt phases matched. DTA/TGA curves for the precipitated phases are given in Figure 3. For nitrate materials, TG-quad indicated that the nitrogen components (such as N_2O , NO , and NO_2) are evolved above $350^\circ C$, indicating that thermal effects below that temperature are caused by dehydration. The mode of decomposition of the nitrate binder is indicated in Graph b of Figure 3, where the material loses water to form $Y_2(OH)_{5.14}(NO_3)_{0.86}$ in the temperature range from 100 to $200^\circ C$. From this point, the thermal decomposition is essentially analogous to that reported²⁰ for $La_2(OH)_{5.1}(NO_3)_{0.9}$, with the endothermal decomposition (DTA peak at $337^\circ C$) leading to $Y_2O_2(OH)_{1.14}(NO_3)_{0.86}$ which then decomposes endothermally (DTA peak at $543^\circ C$) to yttria. Stepwise decomposition

(a) Differential Thermal Analysis of Yttrium Hydroxynitrate Hydrate Binder Phase $[Y_2(OH)_{5.14}(NO_3)_{0.86} \cdot 0.99 H_2O]$ in Argon.

(c) Differential Thermal Analysis of Yttrium Hydroxychloride Hydrate Binder Phase $[Y_2(OH)_{4.86}Cl_{1.14} \cdot 1.07 H_2O]$ in Argon.

(e) Differential Thermal Analysis of Yttrium Hydroxychloride Hydrate Binder Phase $[Y_2(OH)_{4.86}Cl_{1.14} \cdot 1.07 H_2O]$ in Air.

(b) Thermal Gravimetric Analysis of Yttrium Hydroxynitrate Hydrate Binder Phase $[Y_2(OH)_{5.14}(NO_3)_{0.86} \cdot 0.99 H_2O]$ in Argon. [(1) - $Y_2(OH)_{5.14}(NO_3)_{0.86} \cdot 0.99 H_2O \rightarrow Y_2(OH)_{5.14}(NO_3)_{0.86} + 0.99 H_2O \uparrow$; (2) - $Y_2(OH)_{5.14}(NO_3)_{0.86} \rightarrow Y_2O_2(OH)_{1.14}(NO_3)_{0.86} + 2 H_2O \uparrow$; (3) - $Y_2O_2(OH)_{1.14}(NO_3)_{0.86} \rightarrow Y_2O_3 + 0.57 H_2O \uparrow + 0.86 NO_2 \uparrow$ (plus NO and N_2O)]

(d) Thermal Gravimetric Analysis of Yttrium Hydroxychloride Hydrate Binder Phase $[Y_2(OH)_{4.86}Cl_{1.14} \cdot 1.07 H_2O]$ in Argon. [(1) - $Y_2(OH)_{4.86}Cl_{1.14} \cdot 1.07 H_2O \rightarrow Y_2(OH)_{4.86}Cl_{1.14} + 1.07 H_2O \uparrow$; (2) - $Y_2(OH)_{4.86}Cl_{1.14} \rightarrow Y_2O_2(OH)_{0.86}Cl_{1.14} + 2 H_2O \uparrow$; (3) - $Y_2O_2(OH)_{0.86}Cl_{1.14} \rightarrow 0.86 Y_2O_3 + 0.28 YOCl + 0.86 HCl \uparrow$; (4) - $0.86 Y_2O_3 \cdot 0.28 YOCl$]

(f) Thermal Gravimetric Analysis of Yttrium Hydroxychloride Hydrate Binder Phase $[Y_2(OH)_{4.86}Cl_{1.14} \cdot 1.07 H_2O]$ in Air. [(1) - $Y_2(OH)_{4.86}Cl_{1.14} \cdot 1.07 H_2O \rightarrow Y_2(OH)_{4.86}Cl_{1.14} + 1.07 H_2O \uparrow$; (2) - $Y_2(OH)_{4.86}Cl_{1.14} \rightarrow Y_2O_2(OH)_{0.86}Cl_{1.14} + 2 H_2O \uparrow$; (3) - $Y_2O_2(OH)_{0.86}Cl_{1.14} \rightarrow 0.86 Y_2O_3 + 0.28 YOCl + 0.86 HCl \uparrow$ and $0.28 YOCl + 0.07 O_2 \rightarrow 0.14 Y_2O_3 + 0.07 Cl_2 \uparrow$]

Figure 3. DIFFERENTIAL THERMAL AND THERMAL GRAVIMETRIC ANALYSES CURVES FOR TWO YTTRIUM BINDERS IN TWO ATMOSPHERES. (Temperatures Given in Ovals are Extrapolated Points, Indicating Thermal Effects; Temperatures Given in Boxes are Peak Temperatures)

(giving near plateaus on the TGA curves) is thus common to both the precipitated and hydrothermally produced hydroxynitrate phases.

For chloride materials, TG-quad indicated that only water was evolved below 400° C; hydrochloric acid was the only other species detected (above 400° C). Initially, thermal analyses in argon to 1000° C showed that the chloride phases were not completely decomposed. A residue examined by XRD after a 1000° C heating in argon revealed only yttria and an unidentified material (diffraction peaks at 9.4, 4.7, 3.2 and 2.87 Å; the first peak was of medium intensity and the latter three were weak on Debye-Scherrer film). Thermal analyses in argon were extended to 1600° C (as indicated in Graphs c and d, Figure 3), where the endotherm beginning at 1381° C is the only thermal effect not caused by dehydration. Examination of the residue by XRD and chlorine analyses showed that only yttria was present. The results may be explained by the decomposition route illustrated in Graph d, if the endothermal effect above 1381° C results from sublimation of yttrium oxychloride (YOCl or some other complex phase such as $Y_3O_4Cl^{27}$). No plateau region would occur at the yttrium oxychloride composition because of its rapid volatilization by 1430° C. This decomposition route differs somewhat from that proposed by Lance and Haschke²² for $La_2(OH)_{5.1}Cl_{0.9}$ in the region from 300 to 900° C, since they accounted for their observations primarily by water evolution (instead of HCl) to yield lanthanum oxychloride, La OCl.

Since the oxidation of yttrium oxychloride above 800° C had not been studied, thermal studies of the hydroxychloride binder phase were also undertaken in air, as reported in Graphs e and f of Figure 3. It is apparent from Graph e that only the two endotherms from dehydration occur. The sublimation endotherm would not occur if yttrium oxychloride is not present; ie, from oxygen replacement of the chloride ions. This explanation also accounts for the weight-loss data in Graph f. The small deviation in the calculated and observed total weight losses by this route may be caused by some volatilization of yttrium oxychloride.

The reactivities of yttria plasters (both HNO_3 and HCl-produced plasters) were examined, using 7.9 M HNO_3 , 6.05 M HCl, 9.0 M H_2SO_4 , and 7.4 M NH_4OH . The plaster rapidly dissolved in these fairly concentrated nitric acid and hydrochloric acid solutions, but is essentially insoluble in sulfuric acid and ammonium hydroxide solutions (1-hour observation). The minimal reactivity with sulfuric acid is somewhat surprising in view of the conclusion of Mzareulishvili¹⁵ that yttrium hydroxysulfates have a greater tendency to form than hydroxychlorides or hydroxynitrates.

Possible Mechanism of Plaster Formation

Since the "setting" behavior of yttria plaster is so similar to plaster of paris, a mechanism similar to that generally accepted for plaster of paris^{1,2} may be applicable. By analogy, after a fluid slurry of the dilute acid is created, a supersaturation of the liquid with yttrium hydroxysalt binder could occur, followed by precipitation of colloidal binder-phase particles that serve as nuclei for simultaneous deposition and growth of other, larger, binder-phase

crystals. The heat evolution, which occurs a few minutes after mixing, is presumably from rapid dissolution and crystallization. It is possible that the initial acid reaction causes dissolution of yttria (as $YX_3 \cdot nH_2O$, where X represents NO_3^- or Cl^- , and $n \sim 6$), followed by reaction of the soluble salt with yttria to yield the amorphous, sparingly soluble hydroxysalt binder which crystallizes to eventually form the tangled network of randomly oriented, coherent crystals. Although no residual $YX_3 \cdot nH_2O$ phase was detected by XRD analysis, some could have been present below the detection limits.

Materials Incorporation into Yttria Plaster

For various applications, composites with yttria plaster might be required. Thus, several materials were mixed with yttria powder and treated with dilute nitric acid in the same manner as pure yttria.

Oxide additives (nominally > 99 wt % pure) included those listed in Table 4. These plasters were prepared with 2.63 M HNO_3 solutions. Also, niobium metal powder [$- 400$ mesh (or $- 37 \mu\text{m}$)] could readily be incorporated into the yttria plaster. Several concentrations were used, namely: from 10 to 25 wt % Nb, with L/P ratios from 0.3 to 0.8 using a 1.76 M HNO_3 solution.

Table 4
OXIDE ADDITIVES TO
YTTRIA POWDER

Additive	L/P Ratio	Yttria/ Oxide Molar Ratio	Mean Particle Diameter ⁽¹⁾ (μm)
UO_2	0.31	0.5	
	0.46	1.0	21.3
	0.85	2.0	
ZrO_2 (with 5 wt % CaO)	0.56	1.0	12.4
Al_2O_3	0.57	1.0	15.5

(1) Obtained from micromerograph or Coulter Counter.

Yttria Plaster Sinterability Studies

Because of the reticulated structure of yttria plaster and its easy formability, it was considered an ideal candidate for castable, porous refractory insulation. The previously mentioned thermal analyses indicated the encouraging results that the weight loss was gradual. Initial sintering tests with nitric acid-produced plaster in argon used heating rates from 100 to 200°C per hour in the critical region (room temperature to 600°C , the region where maximum evolution of volatiles occurs), with rates from 250 to 500°C per hour above 600°C . These rates were adequate for thin ($< 0.6 \text{ cm}$) specimens. The hydrochloric acid-produced plaster, when sintered to 1350°C in argon, was very friable and exhibited almost no shrinkage. Delayed sublimation of yttrium oxychloride appears to inhibit sintering in argon. Since nitric acid-produced plasters were not friable when sintered to 1350°C in argon, they were further tested. The data are presented in Table 5. The change in microstructure on sintering the HNO_3 -produced plaster is shown in Figure 4 and may be compared to Figure 1 (starting yttria plaster). Thus, the cotton-appearing matrix disappears, with only the needles and plates remaining up to 1350°C , after which the yttria tends to become equiaxed grains.

Sintering of parts thicker than 0.6 cm required a much slower heating rate in the critical region. For a crack-free, 1.3-cm -thick sample of nitric acid-produced plaster, a 10°C -per-hour rate was used to 600°C , followed with a rate of 50°C per hour to 1350°C (a one-hour

(a) At 1100° C.

(b) At 1350° C.

(c) At 1600° C.

Figure 4. CHANGE IN THE MICROSTRUCTURE OF SINTERED YTTRIA PLASTER. (SEM Morphology)

Table 5
CHARACTERIZATION OF SINTERED YTTRIA PLASTER

Condition	Determined by Mercury Intrusion Porosimeter						Linear Shrinkage (%)
	Bulk Density (g/cm ³)	Apparent Specific Gravity ⁽¹⁾	Porosity (%)	Surface Area (m ² /g)	Average Pore Diameter (μm)	Percentage of Pores < 10 μm in Diameter	
Starting Plaster ⁽²⁾	1.13	2.68	57.8	11.8	1.9	100.0	-
Sintered at 1100° C	1.61	5.37	70.1	9.8	2.6	97.3	21
Sintered at 1350° C	2.11	5.08	58.5	1.1	3.1	95.7	25
Sintered at 1600° C	2.35	4.83	51.3	0.3	3.7	98.2	33

(1) Theoretical (X-ray) density of Y₂O₃ is 5.03 g/cm³.

(2) L/P ratio 1.44, using 3.16 M HNO₃.

holding period). A TGA study, with a comparably slow heating rate (30° C/hr) showed that a very uniform rate of evolution of volatiles resulted under these conditions.

Thus, parts that are 1.3 cm in thickness may be sintered, which would be adequate for most uses. If thicker sections are required (ie, for insulation), several thinner sections could be used additively.

Analogous Rare-Earth-Oxide Plasters

Using dilute nitric acid (1.44 M; L/P = 1.0) and freshly calcined (600° C in air) powders, tests showed that several rare-earth oxides (Eu₂O₃, Gd₂O₃, Nd₂O₃, and Sm₂O₃) formed plasters, with the latter two having less strength. With dilute hydrochloric acid (1.1 M; L/P = 1.0) and freshly calcined powders, four other rare-earth oxides (TbO_{1.8-2.0}, Tm₂O₃, Yb₂O₃, and Lu₂O₃) formed plasters, with the latter three having less strength. Although these studies showed that not all rare-earth oxides (or scandium oxide) form plasters, their hydroxysalts (nitrate or chloride) may exist and might be prepared by precipitation, as with yttrium hydroxysalts. The fact that only a few of the rare-earth oxides form plasters may result from kinetic and/or solubility relationships with the hydroxysalts, restricting the formation of interlocking needles or plates.

The europia and gadolinia plasters may be of interest (in the unsintered state) as readily formable neutron-shielding materials.

CONCLUSIONS

A new plaster can be formed by simple reactions of yttria powder with the common acids, rapidly setting into a rigid body consisting of a hydroxysalt binder phase and unreacted

yttria. Resulting plaster bodies can be dried and sintered to form refractory, porous yttria insulation which would be inert to many reactive materials.

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