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CEMENTITIOUS YTTRIA PRODUCTS

C. E. Holcombe

March 1978

OAK RIDGE Y-12 PLANT
OAK RIDGE, TENNESSEE

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ABSTRACT

An investigation has been made of the physical properties and formation conditions of cements formed in the yttria/salt/water system. Cementitious binders were of the nominal $Y_2(OH)_5X \cdot H_2O$ type (where X represents the Cl^- or NO_3^-). An ammonium nitrate-produced yttria cement was shown to be sinterable and was demonstrated to form very refractory castable concretes with zirconia or alumina aggregates.

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SUMMARY

Water-hardenable, yttria-based cements do not result from compositions of yttria with calcia, magnesia, or alumina. The yttria/salt/water system yielded several cement-forming systems, the best of which were with several salts [NH_4NO_3 , $\text{Mg}(\text{NO}_3)_2$, $\text{YCl}_3 \cdot n\text{H}_2\text{O}$ ($n \sim 6$), or NH_4Cl]. A determination was made of the physical properties and formation conditions of these cements. Thermal and X-ray diffraction analyses showed the cementitious binders to be of the nominal $\text{Y}_2(\text{OH})_5\text{X} \cdot \text{H}_2\text{O}$ type (where X represents the Cl^- or NO_3^-) found for yttria plaster. The magnesium nitrate solutions appear to form a new yttrium magnesium hydroxynitrate binder phase. The ammonium nitrate-produced cements were demonstrated to be sinterable and were shown to form a castable concrete, using the zirconia or alumina aggregate.

Several lanthanide oxides (La_2O_3 , Nd_2O_3 , Sm_2O_3 , Eu_2O_3 , and Gd_2O_3) were found to form cements with ammonium nitrate solutions. Also, painted yttria coatings on graphite crucibles could be toughened by forming salt-solution-produced cements.

INTRODUCTION

Since an earlier study of yttria plasters¹ demonstrated the hydration-binding properties possible with yttria, an effort was made^(a) to prepare refractory castable cements and concretes based on yttria. Yttria cement could be used for lining or repairing furnaces or furnace parts to be contacted with reactive materials, as well as for preparing entire furnace assemblies (ie, of concrete).

The only reported^{2,3} yttria-based cements were of the oxide/acid type⁴ and are phosphate systems. Since yttria/acid reactions that involve concentrated acids are difficult to control and handle, this investigation was limited to yttria-based cements hardenable from water alone, or with salt solutions (similar to Sorel cements).

Considerable literature exists on magnesium oxychloride,⁵⁻⁸ illustrating that the formation of mixed oxy-(or hydroxy-) salt binder phases in the magnesia/magnesium chloride/water system produces cements. Since the first part of this study showed that hydroxy-salt binders were formed in yttria/acid/water systems, the yttria/salt/water systems were thought to be worthy of investigation for possible Sorel cement analogs. Ammonium, magnesium, or yttrium salts were selected since ammonia would evolve, magnesia would form (and would not interact with yttria⁹), or yttria would result on sintering.

(a) The work described here was performed by the Development Division of the Oak Ridge Y-12 Plant. This facility is operated by the Union Carbide Corporation-Nuclear Division for the Department of Energy.

NEW YTTRIA CEMENTS

EXPERIMENTAL PROCEDURE

Two grades of (nominally > 99.9 wt % pure) yttria powder were used, as reported in Table 1. The most active (Type A) was used for initial studies on cement formation.

Table 1
DESIGNATION OF YTTRIA POWDERS

Type	Crystallite Diameter (μm)		Agglomerate Diameter (μm)	
	Mean	Range ⁽¹⁾	Mean	Range ⁽¹⁾
A ⁽²⁾	0.06	0.05 - 0.14	3.45	1.59 - 7.26
B ⁽³⁾	7.56	3.51 - 14.95	Minimal Agglomeration	

(1) Upper limit: 90% of the particles are less than the given diameter; lower limit: 10% of the particles are less than the given diameter.

(2) Powder from the Michigan Chemical Corporation, St. Louis, Michigan. Crystallite sizes by electron microscope; agglomerate sizes by Micromerograph.

(3) Powder from the Research Chemical Corporation, Phoenix, Arizona. Crystallite sizes by Coulter Counter.

To study cement formation, enough liquid was added to the powder to ensure uniform mixing. The liquid-to-powder (or L/P) ratios^(b) adequately define the compositions used. Freshly calcined (30 minutes at $\sim 600^\circ\text{C}$ in air) powders were used. Samples were mixed in glass beakers. After mixing, the beakers were supported in a sealed bottle containing a saturated ammonium sulfate solution, which provided a curing environment with a fixed 81.1% relative humidity (RH). Samples were inspected frequently for the first 48 hours and observed intermittently for approximately 30 days to detect any hardening tendencies during curing. At the end of this time period, samples were dried at $50 - 60^\circ\text{C}$ in air for 24 - 48 hours and examined by scanning electron microscopy (SEM).

For water-hardenable yttria-based cements, compositions in the $\text{CaO}/\text{Y}_2\text{O}_3$, $\text{MgO}/\text{Y}_2\text{O}_3$, $\text{Al}_2\text{O}_3/\text{Y}_2\text{O}_3$, and $\text{CaO}/\text{Al}_2\text{O}_3/\text{Y}_2\text{O}_3$ systems were thought to be good candidates for cement formation. Attempts were made to prepare compounds with the following formulae: CaY_2O_4 , CaY_4O_7 , $\text{Ca}_3\text{Y}_2\text{O}_6$, $\text{Mg}_3\text{Y}_2\text{O}_6$, $\text{Al}_2\text{Y}_4\text{O}_9$, $\text{Al}_{10}\text{Y}_6\text{O}_{24}$, and $\text{CaAl}_2\text{Y}_2\text{O}_7$. Reagent-grade magnesia, calcia, and aluminum nitrate nonahydrate were added to yttria in the correct molar ratios to produce the desired nominal formulae on sintering. The powder mixtures were then completely dissolved in nitric acid solutions and precipitated by adding the solution dropwise to an excess of ammonium hydroxide. After filtering and washing the precipitates with water, the mixed hydroxides were dried ($50 - 60^\circ\text{C}$ for 24 hr) and heated to $1000 - 1100^\circ\text{C}$ for 4 - 5 hours in alumina crucibles. Each composition was tested for cement formation in the same manner as for the yttria/salt/water samples. Depending on the sample, L/P ratios of 0.6 to 1.2 were used.

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

For initial yttria/salt/water studies, a salt^(c) solution (representing the liquid in the L/P) was prepared at a concentration fairly close to saturation (except for ammonium nitrate which has much greater solubility in water than the others tested). Concentrations are generally reported in molarity^(d) since solutions could be readily prepared with that information. Approximate molarities^(e) are given for the more promising salt solutions (based on the observation of the volume increase on adding the salt to water). Several salts were investigated [NH_4NO_3 , NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_2\text{CO}_3$, $\text{Mg}(\text{NO}_3)_2$, MgCl_2 , MgSO_4 , $\text{Y}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$, and $\text{YCl}_3 \cdot n\text{H}_2\text{O}$].^(f)

Five lanthanide oxides (La_2O_3 , Nd_2O_3 , Sm_2O_3 , Eu_2O_3 , and Gd_2O_3) with the system lanthanide oxide/ammonium nitrate/water were also examined for cement formation.

The characterization techniques (scanning electron microscopy, X-ray diffraction, porosimeter, and thermal analyses) were as described previously.¹ Approximate time of set for these cements was qualitatively determined as the time when the surface became difficult to penetrate with a spatula blade. Relative hardness was also noted.

RESULTS AND DISCUSSION

Neat Yttria Cements

These studies on possible water-hardenable, yttria-based compositions were generally unsuccessful. The only compounds with yttria that were detected by X-ray diffraction after calcining were $\text{Al}_2\text{Y}_4\text{O}_9$ (or $\text{Al}_2\text{O}_3 \cdot 2\text{Y}_2\text{O}_3$) and $\text{Al}_{10}\text{Y}_6\text{O}_{24}$ (or $3\text{Y}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$), with the other compositions being mixtures of the respective starting oxides. Of the samples examined, only the $3\text{MgO} \cdot \text{Y}_2\text{O}_3$ showed hardening tendencies—from $\text{Mg}(\text{OH})_2$ by X-ray diffraction.

The initial screening data on cement formation in the yttria/salt/water systems are given in Table 2. The samples prepared with sulfates and $\text{Y}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$, although forming cements, cracked badly on drying. The magnesium chloride sample did not set up, and the ammonium carbonate sample set up weakly, resembling chalk after drying. Several samples were set up with minimal or no cracking [formed from NH_4NO_3 , $\text{Mg}(\text{NO}_3)_2$, $\text{YCl}_3 \cdot n\text{H}_2\text{O}$, and NH_4Cl salt solutions], and were examined by X-ray step-scanning techniques. The X-ray diffraction pattern of cements produced from ammonium nitrate solution showed yttria and the nominal $\text{Y}_2(\text{OH})_5\text{NO}_3 \cdot \text{H}_2\text{O}$ phase reported previously.¹ Also, the X-ray diffraction patterns of cements produced from ammonium chloride and $\text{YCl}_3 \cdot n\text{H}_2\text{O}$ were accounted for by yttria and the nominal $\text{Y}_2(\text{OH})_5\text{Cl} \cdot \text{H}_2\text{O}$ phase previously reported.¹ From relative peak intensities, the unreacted yttria generally appeared to be the major phase for reasons

(c) Reagent-grade salts were used.

(d) Defined as moles of solute per 1000 grams of solvent (water).

(e) Defined as moles of solute per liter of solution.

(f) Where $n = \sim 6$. Salts were prepared as described previously.¹

Table 2
SALT SOLUTIONS TESTED FOR CEMENT FORMATION WITH YTTRIA

Salt ⁽¹⁾	Concentration of Salt Solution (m)	L/P Ratio ⁽²⁾	Approximate Time for Initial Set	Effect of Drying (at 50° C for 24 - 48 hrs)	Percent Linear Drying Shrinkage (for 2.25-cm samples)	General Comments	Scanning Electron Microscopy Observations ⁽³⁾
NH ₄ NO ₃	13.9	0.6	< 48 Hr	No Cracks	~ 0	Very hard after drying.	0.75 - 1.75 μ m <u>plates</u> and needles present as the bonding phase.
NH ₄ Cl	6.9	0.75	~ 4 Wk	No Cracks	~ 5	Weakly set, but becomes very hard on drying.	0.25 - 1 μ m <u>plates</u> and needles as the bonding phase.
(NH ₄) ₂ SO ₄	5.5	0.6	< 48 Hr	Cracked	-	-	2.5 - 10 μ m <u>chunky</u> particles.
(NH ₄) ₂ CO ₃	5.5	0.75	~ 4 Wk	No Cracks	~ 0	Weakly set; resembles chalk.	0.5 - 2 μ m <u>needles</u> as the bonding phase.
Mg(NO ₃) ₂	4.4	0.6	< 1 Wk	Few Cracks on Top	~ 4	Very hard after drying.	4 - 13 μ m <u>chunky</u> particles.
MgCl ₂	2.7	0.75	No Set	-	-	Not hard after drying.	3 - 12 μ m <u>chunky</u> particles.
MgSO ₄	3.5	0.8	< 2 Wk	Cracked	-	-	2.5 - 7.5 μ m <u>chunky</u> particles.
Y(NO ₃) ₃ ·nH ₂ O	1.4 $\left(\begin{smallmatrix} \text{based on} \\ n = 6 \end{smallmatrix} \right)$	0.8	< 1 Wk	Badly Cracked	-	Cracked before drying after ~ 1 wk.	1.25 - 3.4 μ m <u>plates</u> and needles as the bonding phase.
YCl ₃ ·nH ₂ O	1.3 $\left(\begin{smallmatrix} \text{based on} \\ n = 6 \end{smallmatrix} \right)$	0.65	< 48 Hr	No Cracks	~ 0	Hardening begins at ~1 hr; very hard after drying.	0.25 - 0.75 μ m <u>plates</u> and <u>needles</u> as the bonding phase.

(1) Conditions after blending with Y₂O₃ powder (Type A) and exposing to a 81.1% relative humidity [from a saturated (NH₄)₂SO₄ solution].

(2) Liquid volume (in cm³)/powder weight (in grams).

(3) Dimensions are diameter (for plates), lengths (for needles), or largest dimension (for particles). These are approximate ranges; primary shape of particles is underlined.

discussed before.¹ The X-ray diffraction pattern of the cement prepared from magnesium nitrate is shown in Table 3 and represents an unidentified binder material—probably a yttrium magnesium hydroxynitrate, since no free magnesium nitrate was detected.

The physical properties of dried yttria-based cements are reported in Tables 4 and 5. The measured porosity values are much lower than for plasters (generally 50 to 65%), and were regularly less than 50%. The relative hardnesses of these cements paralleled the porosity trends. Although magnesium nitrate-produced cements were quite hard, they always cracked on drying (for ~13-mm-thick samples). For concrete, where only a thin cementitious layer is required between inert aggregates, the magnesium nitrate-produced cements may be used without cracking occurring.

Table 5 also illustrates the effect of varying the ammonium nitrate concentration and the yttria particle size. For an $L/P = 0.7$, a theoretical concentration of 6.3 molar (M) would give complete conversion to the nominal binder phase composition: $Y_2(OH)_5NO_3 \cdot H_2O$. However, an ~8.5- M solution of ammonium nitrate yielded only 87% conversion to the binder phase. It is suspected that the degree of binder formation depends on the difference between the initial concentration of the salt in solution and a final equilibrium concentration of the salt in solution. For this reason, excess ammonium nitrate (over the theoretical required to form the hydroxynitrate binder) is beneficial in yielding a higher percentage of the binder phase in the cement. The physical-property variation with salt-solution concentration is further illustrated in Figure 1. From Table 5 and Figure 1, a concentration of 13.9 molal (m) seems to provide a good balance between excess ammonium nitrate and porosity of the dried cement.

The ammonium nitrate concentration may fall in the range of 0.7 to 23.3 M . If the concentration is $\leq 0.4 M$, the cement will not set up. At 23.3 m , the liquid phase is

Table 3
X-RAY DIFFRACTION PATTERN OF CEMENT FORMED
BY THE ADDITION OF MAGNESIUM NITRATE
SOLUTION (4.4 m) TO YTTRIA POWDER

d spacings (Å)	I/I ₁₀₀ ⁽¹⁾	I/I ₁₀₀ ⁽²⁾
10.33	18	100
9.11	8	44
8.75	4	22
8.54	3	17
8.34	4	22
7.89	3	17
4.34	10	
3.07	100	
2.66	24	
2.50	5	
2.38	< 1	
2.27	6	
2.17	< 1	
2.08	8	
1.941	3	
1.879	43	
1.822	2	
1.724	5	
1.682	1	
1.639	4	
1.615	28	
1.565	5	
1.534	4	
1.502	2	
1.472	1	
1.445	3	
1.419	1	
1.348	2	
1.327	4	
1.308	3	
1.295	1	
1.269	2	
1.252	1	
1.234	1	
1.218	6	

(1) Peak-height intensities, diffractometer, copper $K\alpha$ radiation.

(2) Excluding yttria spacings.

Table 4
PHYSICAL PROPERTIES OF SOME NEAT YTTRIA CEMENTS PREPARED WITH SALT SOLUTIONS

Salt (1,2)	Concentration of Salt Solution (3) (m)	Powder Type (4)	Bulk Density (g/cm ³)	Apparent Specific Gravity	Porosity (%)	Surface Area (m ² /g)	Average Pore Diameter (μm)	Percentage of Pores Less Than 10 μm Diameter (%)	Total Percentage Weight Lost on Heating to 1500° C in Argon (5) (%)
NH ₄ Cl	6.9 [~ 4.6]	A	1.89	3.03	37.7	23.6	0.3	99.3	29.5
Mg(NO ₃) ₂	4.4 [~ 3.7]	A	2.48	3.19	22.1	0.5	3.1	95.2	27.5
Mg(NO ₃) ₂	4.4 [~ 3.7]	B	2.19	3.36	34.9	0.5	2.2	99.0	
YCl ₃ ·nH ₂ O (n = ~ 6)	1.3 [~ 1.2]	A	1.62	3.16	48.7	45.0	0.2	99.7	23.5

(1) Cements prepared with L/P = 0.6 - 0.75, cured 30 days, dried.

(2) Properties determined with mercury intrusion porosimeter.

(3) Approximate molarities shown in brackets.

(4) See Table 1 for identification.

(5) By thermogravimetric analyses.

Table 5

COMPARISON OF NEAT YTTRIA CEMENTS PREPARED WITH DIFFERENT AMMONIUM NITRATE CONCENTRATIONS AND PARTICLE SIZES

Concentration of NH_4NO_3 ^(1,2) (<u>m</u>)	Powder Type ⁽³⁾	Bulk Density (g/cm ³)	Apparent Specific Gravity	Porosity (%)	Surface Area (m ² /g)	Average Pore Diameter (μm)	Percentage of Pores Less Than 10 μm Diameter
3.1	B	1.41	3.19	55.7	18.7	0.9	98.8
12.5	B	1.77	3.08	42.5	14.8	1.0	97.6
13.9 [~ 8.5] ⁽⁴⁾	B	1.84	2.95	37.6	11.4	0.8	99.1
23.3 ⁽⁵⁾	B	1.95	2.71	27.9	5.0	0.2	99.8
13.9	A	1.94	2.79	30.4	15.9	0.1	100.0
23.3 ⁽⁵⁾	A	1.97	2.81	29.7	7.5	1.1	97.7

(1) Cements prepared with an L/P = 0.7, cured 30 days, dried.

(2) Properties determined by mercury intrusion porosimeter.

(3) See Table 1 for identification.

(4) Specimen analyzed by quantitative X-ray diffraction analysis showed 13 ± 3 wt % free yttria; by thermogravimetric analysis, 33.8 wt % lost on heating to 1500° C in argon; approximate molarity shown in brackets.

(5) Saturated solution; molarity shown represents solubility at 21.1° C. The solubility varies [ie, from 22.7 m (20° C) to 24.0 m (22.2° C)] with room temperature.

saturated and causes setting, but is rather difficult to handle because of the excess ammonium nitrate. The L/P ratio generally used for yttria cement was 0.6 to 0.8. If excess liquid is used, the cement sets up under the excess liquid; if too little is used, a stiff, nonworkable paste results. Generally, the lower L/P limit appears to be ~ 0.5 .

The mechanism of cement formation is probably very similar to that suggested for plaster formation. The major difference appears to be kinetics. Use of salt solutions appears to slow down the rate of formation of the binder-phase crystals (generally needles or plates) in such a fashion that a much greater packing density occurs, giving rise to the low-porosity, hard cements. It should be noted that, regarding both plasters and cements, yttria is never completely converted to the hydroxy-salt binder. Therefore, the neat^(g) cements are really concretes with the residual unreacted yttria acting as an aggregate.

Simultaneous differential thermal analysis/thermal gravimetric analysis (DTA/TGA) in flowing argon and complementary thermogravimetric (TG)-quad analyses [at a pressure of $< 10^{-4}$ torr ($< 1.33 \times 10^{-2}$ Pa)] were undertaken to 1000° C for each of these cements [prepared from NH_4NO_3 , $\text{Mg}(\text{NO}_3)_2$, $\text{YCl}_3 \cdot n\text{H}_2\text{O}$, and NH_4Cl]. The decomposition processes and thermal effects for the ammonium nitrate-produced cement are identical to those previously discussed¹ for nitric acid-produced plaster and yttrium hydroxynitrate hydrate binder phase, with the exception that some evolution of the N-H-O species (NH_3 , N_2 , NO , N_2O , NO_2) below 200° C occurred from excess ammonium nitrate. [The TG-quad analysis of pure ammonium nitrate indicated that it decomposes completely by the time a temperature of 160° C is reached.]

(g) The term "neat" refers to materials having a zero aggregate content.

Note: Data from samples used in Table 5 plus additional samples prepared in the same manner.

Figure 1. VARIATION IN THE PHYSICAL PROPERTIES OF AMMONIUM NITRATE-PRODUCED CEMENT WITH CONCENTRATION OF THE SALT SOLUTION. [Cements Prepared with an L/P = 0.7 (Type B powder), Cured for 30 Days, then Dried]

Thermal analyses of the yttrium chloride hexahydrate and ammonium chloride-produced cements matched those reported previously¹ for yttrium hydroxychloride hydrate binder phases in argon. No ammonia was detected by TG-quad, since no excess ammonium chloride was used over the theoretical for forming the binder.

The DTA/TGA curves for magnesium nitrate-produced cements further pointed out that a discrete new phase had formed since they did not match the DTA data for the hydroxynitrate binder. Figure 2, Graphs a and b, illustrate its decomposition behavior to 1000° C. No additional thermal effects occurred to 1500° C. The TG-quad study to 1000° C showed that only water evolved below 350° C; above 350° C, N-O species (NO, N₂O, NO₂) were liberated. This result establishes that endotherms below 350° C arise from dehydration. Since TG-quad data were taken in vacuum, species generally evolve at somewhat lower temperatures than would result in argon; thus, both endotherms observed in argon above 350° C may occur from N-O species, or only the higher-temperature endotherm could result

from evolution of N-O species as for yttrium hydroxynitrate binder. The higher-temperature endotherm (beginning at $\sim 473^{\circ}\text{C}$) peaks at a point similar to that for yttrium hydroxynitrate binder, probably since these nitrate phases appear to be unstable above 600°C .

Thermal analyses indicated that the nitrate cements could be sintered if a sufficiently slow heating rate was used below 600°C . The chloride cements, from thermal data, could be sintered in air (because of replacement of the chlorine with oxygen discussed before¹), but sintering in argon would be hampered by rapid yttrium oxychloride evolution above 1400°C (after structural development has taken place). Sintering the cement produced from a magnesium nitrate salt solution would result in a mixture of yttria and magnesia⁹ which could have a relatively high expansion coefficient—the weighted average of yttria ($\sim 8 \times 10^{-6}/^{\circ}\text{C}$, to 1000°C) and magnesia ($\sim 14 \times 10^{-6}/^{\circ}\text{C}$, to 1000°C) phases. For some applications for matching the expansive behavior of substrates, the magnesium nitrate-produced yttria cement may be advantageous. One decisive advantage of yttria cements over conventional castable cements (ie, calcium aluminates) is that yttria cements are not subject to rehydration after sintering.

The physical properties of neat ammonium nitrate-produced yttria cement before and after sintering ($\sim 0.6\text{-cm-thick}$ specimens) are reported in Table 6. Figure 3 illustrates the microstructural changes that result from sintering. The data indicate that the bulk-density values before and after sintering are considerably higher (and the porosities considerably lower) than yttria plaster. Yttria cement is about 40 to 50% more dense than the plaster. The acicular (needlelike) or lenticular (platelike) crystals appear to be quite compact in View a of Figure 3, and little resemblance of the original structure remains at 1350°C (View b). However, other than denseness of the particle packing, the morphology of the yttria cement on sintering parallels that of yttria plaster.

Analogous Lanthanide Cements

The hydroxychloride and hydroxynitrate binder phases, as shown for yttria plasters, would be expected to exist for the rare-earth oxides. Thus, a study was made of the behavior of those oxide powders already discussed (La_2O_3 , Nd_2O_3 , Sm_2O_3 , Eu_2O_3 , and Gd_2O_3) with ammonium nitrate solutions. The physical properties of these neat cements are given in Table 7. The cements tested had similar properties except lanthania which expanded on curing and (by SEM) formed very large particles (typically, $5\text{ }\mu\text{m}$ long by 1 to $2\text{ }\mu\text{m}$ wide)—primarily appearing as multiple plates bonded into a needle shape.

Preparation of Concrete—Effects of Oxide Additives to Yttria Cement

Preparation of a castable concrete based on yttria has the advantage of allowing the formation of a thin cement (or binder phase) layer between the aggregate particles, aiding sinterability (without cracking), and allowing the properties of the composite to be tailored for specific needs. The effects of aggregates were tested by using 80 wt % aggregate and 20 wt % yttria with a 13.9M ammonium nitrate solution ($\text{L/P} \leq 0.2$, generally). Of several

Figure 2. THERMAL ANALYSES OF CEMENT FORMED BY THE ADDITION OF MAGNESIUM NITRATE SOLUTION TO YTTRIA POWDER. (Temperatures Given in Ovals are Extrapolated Points, Indicating Thermal Effects; Temperatures Given in Rectangles are Peak Temperatures)

Table 6
COMPARISON BETWEEN AS-FORMED AND SINTERED
NEAT AMMONIUM NITRATE-PRODUCED
YTTRIA CEMENT

	As Formed(1,2)	Sintered(3)
Linear Shrinkage (%)	~ 0	~ 18
Bulk Density (g/cm ³)(4)	1.94	2.89
Apparent Specific Gravity(5)	2.79	4.96
Porosity (%)	30.4	41.7
Surface Area (m ² /g)	15.9	1.85
Average Pore Diameter (μm)	0.1	0.5
Percentage of Pores Less Than 10 μm Diameter	99.98	99.34

- (1) Cement prepared from 13.9-m NH₄NO₃, with L/P = 0.6, using Type A powder.
- (2) Cured for 30 days, then dried at 50° C for 24 - 48 hours.
- (3) Heated at 35° C/hr to 600° C; 175° C/hr from 600 to 1350° C, held for 15 min at 1350° C; cooled to RT in ~ 4 hr; argon atmosphere.
- (4) All values except linear shrinkage were determined by the mercury intrusion porosimeter.
- (5) Theoretical (X-ray) density of yttria is 5.03 g/cm³.

(a) As formed, dried (50° C).

(b) Sintered (1350° C).

Figure 3. CHANGES IN THE MICROSTRUCTURE OF YTTRIA/AMMONIUM NITRATE CEMENT ON SINTERING. (SEM Morphology; Figure Widths of the Photomicrographs Represent ~ 11 μm)

Table 7
PHYSICAL PROPERTIES OF NEAT LANTHANIDE CEMENTS

Property ^(1,2)	Starting Oxide ⁽³⁾					Comments
	La ₂ O ₃ ⁽⁴⁾	Nd ₂ O ₃	Sm ₂ O ₃	Eu ₂ O ₃	Gd ₂ O ₃	
Hardness Rank ⁽⁵⁾	5	1	4	2	3	No cracking was observed during curing or after drying. Drying shrinkage was ~ 0 for 2.25-cm samples. Each oxide appeared to begin reacting shortly after mixing, since some ammonia evolved and heating occurred.
Approximate Time for Initial Set	< 24 hr	< 48 hr	< 2 wk	< 48 hr	< 48 hr	
Bulk Density (g/cm ³)	1.43	1.82	1.87	1.80	1.80	
Apparent Specific Gravity	3.09	3.46	3.45	3.37	3.51	
Porosity (%)	53.8	47.4	45.8	46.6	48.7	
Surface Area (m ² /g)	3.6	11.0	5.6	11.3	12.6	
Average Pore Diameter (μm)	1.9	0.3	1.4	0.4	0.7	
Percentage of Pores Less Than 10 μm Diameter	98.3	99.5	99.0	99.5	99.1	

(1) Cements prepared from 13.9-m NH₄NO₃ with L/P = 0.8; cured 30 days.

(2) Properties determined by mercury intrusion porosimeter with dried (50 - 60° C, 24 - 48 hr) samples.

(3) Nominally < 500 mesh (or < 25 μm) and > 99 wt % pure.

(4) Cement expanded during drying, breaking the glass container after five days.

(5) Determined before and after drying. Ranks 1 - 3 are quite hard; Ranks 4 and 5 are moderately hard.

aggregates (Al₂O₃, SiC, MgO, and CaO-stabilized ZrO₂; nominally -14 +325 mesh or -1410 +44 μm particle size), zirconia allowed the formation of the hardest, tough concrete, setting in 24 - 72 hours. This material appeared to become harder on drying at 50° C for 24 hours. However, after about two days of an additional exposure to air (~ 50% RH) at room temperature, the strength of the concrete deteriorated. Examination by the SEM showed that the needle (or plate)-like phase was bonding to the zirconia particles, but microcracking had resulted (presumably from rehydration). Thus, this concrete should be sintered as soon as possible after initial drying to prevent microcracking.

The alumina aggregate formed a weaker concrete than zirconia. Aggregates of silicon carbide yielded a relatively weak concrete (possibly because of the aggregate-to-yttria ratio of 4 to 1). The magnesia aggregate prevented setting, although some strength developed on drying.

Crucibles (~ 5" D x ~ 5" H, with ~ 0.5" walls) of 20 wt % yttria/80 wt % aggregate were prepared with a 13.9-m ammonium nitrate solution. Both zirconia and alumina were used as aggregates. After curing (36 hr in 100% RH) and drying (50° C, 15 hr), the crucibles were sintered in vacuum (1.33 x 10⁻² Pa)—yttria/alumina at 1600° C for 2 hr; yttria/zirconia at 1950° C for 1 hr. Heating rates of 100° C/hr to 600° C were used to allow volatile material from the hydroxysalt binder phase to escape without cracking the crucibles. Above 600° C and for cooldown, rates of 250 - 400° C/hr were used. Using these procedures, tough, well-sintered, yttria-based concrete crucibles resulted.

Hardening Yttria Coatings on Graphite

Yttria-paint protective coatings for graphite crucibles have been previously developed, using a 3% sodium carboxymethylcellulose (CMC) solution¹⁰ as the suspension agent, binder, and sintering aid. Generally, L/P ratios of 1.0 to 1.9 were used. Since the yttria/salt/water-type

cements set fairly slowly (compared to yttria plasters), consideration was given to the possibility of toughening the coatings for preventing or reducing flaws resulting from crucible-loading operations. It was found that these brush-applied coatings may be hardened by: (1) spraying the finished coating with a dilute ammonium nitrate solution, such as 0.7 m (the lower initial concentrations are favored, since the final concentration increases on drying), or (2) adding ammonium nitrate to the 3% CMC solution, followed by mixing the paint normally [$\leq 0.7 \text{ m NH}_4\text{NO}_3$ works well; lower concentrations permit longer handling times (pot life) of the paint before setting commences]. The coatings must then be cured for about 7 - 10 days in normal room air ($\sim 50\%$ RH) to achieve the maximum benefit to the unsintered coating (paint) on graphite. The curing time of up to 10 days in room air was found necessary for other ammonium nitrate-produced yttria cements, as compared to the 24 - 48-hour time span for adequate curing in an 81.1% RH environment.

CONCLUSIONS

A new cement can be formed from the simple reaction of yttria powder with salt solutions. The cement has porosities in the range of 20 - 50% (typically 30 - 40%), which is 25 to 60% lower in porosity than for acid-produced yttria plasters. Sinterable concretes may be prepared with alumina (usable to $\sim 1650^\circ \text{C}$) or zirconia (usable to $\sim 2000^\circ \text{C}$) aggregates, with the latter forming a concrete which can be used about 400°C above the maximum use temperature of calcium aluminate-based concretes. Thus, yttria-based concretes are not subject to rehydration, and (since only $\sim 20 \text{ wt } \%$ is used for the cementitious yttria constituent) provides a relatively inexpensive, high-temperature castable that is applicable for many structural uses (eg, crucibles and supports) in reactive environments. The yttria/zirconia composition should be useful for high-temperature corrosive environments (ie, magnetohydrodynamic generator applications).

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