Ni–Al–Ta system. Dendritic monocrystals of various compositions are sectioned at different locations from the quenched interface and temperature at the moment of quench, corresponding at the boundaries limiting the γ'-precipitated regions are subsequently established by electron microprobe analysis. Temperature is finally plotted versus concentration of each solute and results are reported on the ternary diagram.

The accuracy of the method is estimted to ± 3° C in temperature and ± 0.05 of 1% in concentration. The method is general in nature, rapid and allows the construction of a solvus curve with only one dendritic monocrystal of a given composition.

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New magnesium hydroxynitrate hydrate binder

Nitrate-based magnesia cements have been rarely reported [1, 2], and only one magnesium hydroxynitrate composition, $Mg_3(OH)_4(NO_3)_2$, has been defined [3] – resulting from thermal decomposition of $Mg(NO_3)_2 \cdot 6H_2O$ above 300° C.

This study was undertaken to examine nitrate-based cements formed from magnesia (MgO) powder. The MgO powder was $\geqslant 99.86$ wt% pure by spark-source mass spectrometry, and had a mean particle diameter of 4.2 μm. The solutions used were reagent grades of $Mg(NO_3)_2$, NH_4NO_3, or HNO_3 and are shown in Table I along with observations of cement formation. The MgO powder (pre-calcined at 600° C) was mixed with the appropriate solution in a glass beaker. The liquid volume in cm^3 to powder weight in grams (or L/P) ratios adequately define the compositions used. After mixing, the beakers were held by a larger beaker in a sealed container of saturated $(NH_4)_2SO_4$ solution which provided a curing environment with a fixed 81.1% relative humidity. Samples were inspected frequently for 72 h and intermittently observed for 2 weeks. Afterwards, samples were dried at 50° C for 24 to 48 h, and examined by X-ray diffraction (XRD).

Table I shows that the same phase (unknown "X") occurs for all $Mg(NO_3)_2$ additions to MgO. Only slight variations in intensity occurred in the XRD patterns. The cements which set and could be dried without cracking (Nos. 1 and 2) were analysed chemically and by mercury intrusion porosimetry, with the data presented in Table II.

Since the predominant phase from HNO_3 or NH_4NO_3 reactions is $Mg(OH)_2$, and since there is considerably less NO_3^- present in the dried cements than initially used, it appears that some nitrogen components (such as N_2O, NO, NO_2) must be evolved in the formation of the binder, such that its final composition is approximately constant whenever $Mg(NO_3)_2$ salt solutions are used. The slight intensity variations in the XRD data probably result from variable water content. The $Mg(OH)_{1.8}(NO_3)_{0.2} \cdot 1.55\ H_2O$ binder phase XRD pattern is shown in Table III.

Examination of the cementitious $Mg(NO_3)_2$-produced materials by scanning electron microscopy showed the binders to be needles (1 to 15 μm

TABLE I Solutions tested with magnesium oxide

Cement number	Cement formation conditions[1]				Curing observations	Drying observations[5]	X-ray diffraction[6]
	Material in solution	Concentration of solution (M [m])[2]	L/P ratio[3]	Initial NO_3^-/Mg^+ ratio[3]			
1	$Mg(NO_3)_2$	3.7 [4.4]	3.4	0.67	[4] Set in 24 h	Very hard, uncracked	Unknown "X"
2		3.7 [4.4]	2.2	0.50	Very hard at 72 h	Very hard, uncracked	"X"
3		3.7 [4.4]	1.6	0.38		Badly cracked	"X"
4		3.1 [4.4]	1.6	0.33		Badly cracked	"X"
5	NH_4NO_3	9.3 [17.0]	1.6	0.60	Set in ~ 72 h, resembling soapstone	Uncracked, as soapstone	Major phases: $Mg(OH)_2$, NH_4NO_3 Minor phase: unidentified
6	HNO_3	3.2	1.6	0.20	Set in ~ 24 h, with surface cracking	Surface cracked	$Mg(OH)_2$

[1] Prepared by blending the solutions with MgO powder (in a glass container) and curing in 81.1% relative humidity [from a saturated $(NH_4)_2SO_4$ solution] for 2 weeks.

[2] Molarity with molality (moles of salt per 1000 g of water) in brackets.

[3] Liquid volume in cm^3, powder weight in g.

[4] Cement No. 1 expanded during curing, breaking the inner glass container after 48 h.

[5] After 24 to 48 h at 50° C.

[6] Debye–Scherrer film, CuKα radiation; from dried samples

TABLE II Properties of magnesium hydroxynitrate hydrate binder phase

Property	Cement number	
	1	2
Formula by chemical analyses for Mg, O, N, and H *	$Mg(OH)_{1.82}(NO_3)_{0.18} \cdot 2.14 - 2.25\ H_2O$	$Mg(OH)_{1.80}(NO_3)_{0.20} \cdot 1.51 - 1.58\ H_2O$
Final NO_3^-/Mg^+ ratio	0.18	0.20
Bulk density, † ($g\,cm^{-3}$)	1.33	1.33
Apparent specific gravity†	2.05	2.05
Porosity (%) †	35.1	35.1
Surface area †	9.2	12.7

*Elemental analyses were adjusted to the formula $Mg(OH)_{2-m}(NO_3)_m \cdot n\ H_2O$; water contents were calculated from remaining oxygen and from the total difference necessary for 100% when summing constituents; both values are given.
†Determined by mercury intrusion porosimetry.

long by 0.05 to 2 μm wide). The average pore diameters were < 1 μm with 98.8% of the pores < 10 μm, as determined by porosimetry.

TABLE III X-ray diffraction patterns of $Mg(OH)_{1.8}(NO_3)_{0.2} \cdot 1.55\ H_2O$ binder phase*

d-spacings (A°)	I/I_{100}†	d-spacings (A°)	I/I_{100}†
9.16	1	2.28	4
8.34	18	2.20	4
6.89	8	2.09	24
6.66	2	2.05	1
6.11	14	1.977	1
5.96	2	1.922	15
5.12	2	1.880	<1
4.95	100	1.827	5
4.44	< 1	1.724	5
4.19	8	1.670	3
3.92	3	1.616	1
3.65	1	1.590	1
3.59	3	1.575	4
3.45	11	1.551	1
3.34	1	1.530	2
3.22	1	1.501	7
3.08	1	1.443	1
3.00	27	1.403	<1
2.87	6	1.388	<1
2.79	6	1.373	<1
2.73	< 1	1.341	3
2.68	8	1.285	<1
2.57	< 1	1.259	1
2.53	9	1.232	1
2.47	55	1.212	<1
2.37	1	1.193	<1

*Formula based on chemical analysis of Cement No. 2 with water content representing the average calculated from remaining oxygen or by difference (See Table II).
†Peak height intensities, diffractometer, radiation.

Thermal decomposition of $Mg(OH)_{1.8}(NO_3)_{0.2} \cdot 1.55\ H_2O$ (Cement No. 2) was studied by thermal analyses (DTA–TGA in argon and TG-quadrupole mass spectographic analysis in vaccuum) as described for yttrium hydroxysalt phases [4]. The TG-quad indicated N–O species occur predominantly ⩾ 175° C. By DTA, two endotherms occur – 112 to 285° C (161° C peak) and 370 to 528° C (480° C peak). By TGA, 17.3% weight loss occurred from room temperature to 285° C (where the weight stabilized), and 41.6% loss occurred from 370 to 528° C, accounting for the total 58.9% weight loss. The theoretical weight loss in forming MgO from $Mg(OH)_{1.8}(NO_3)_{0.2} \cdot 1.55\ H_2O$ is 57.7%. The TG-quad data indicate that the first endotherm could result from dehydration above, which would yield $Mg(OH)_{1.8}(NO_3)_{0.2} \cdot 0.635\ H_2O$.

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