

# GREEN COLD CRUSHING STRENGTH DEVELOPMENT AND HYDRATION RESISTANCE OF ALUMINA-MAGNESIA CASTABLE IN THE FIRST 24 HOURS OF CURING: THE EFFECT OF THE BINDER TYPE, MAGNESIUM OXIDE PARTICLE SIZE AND ADDITIVE PACKAGE

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## ABSTRACT

The alumina-magnesia castables, in order to be used as a precast material for the steel industry in applications such as well blocks, RH snorkels and impact pads, must attend some specifications: fast development of mechanical resistance in a green state and high slaking resistance. Based on this assumption, a product was developed to attend these specifications (6% cement and 6% fine magnesia). However, this same product showed problems due to cracks after drying even though the performance was very good.

After an investigation considering the main variables (process and product) a new product was developed without the problems mentioned before. This new product was based on a combination of cement or hydratable alumina, coarse magnesia and an appropriate additive package. The system with hydratable alumina has the advantage of presenting a higher GCCS in the first 24 hs of curing.

## INTRODUCTION

Alumina-magnesia low cement castables have been widely used as precast blocks in Brazil, mainly as steel ladle well blocks and snorkel degasser. The success of these products is related to their less slag corrosion, less slag infiltration and reasonable performance against oxygen cleaning when compared to high alumina and alumina-spinel based products. The relative lower cost of magnesia sinter in comparison with spinel has also to be considered.

At the beginning of the production of precast shapes with alumina-magnesia castables in our company, fine magnesia was used. Although the green strength and performance was considered very good, it was very difficult to establish a defect-free production of such material, due to the cracking phenomenon during drying-out step in the production process. Since 2006 we have changed the magnesia grain size and the additive package. This has completely eliminated the cracking phenomenon during the drying-out step, although the mechanical resistance after 24 hs is relatively low requiring careful handling. In order to improve the earlier green strength studies have being doing with hydratable alumina.

The main objective of the present work was to improve the mechanical strength within the first 24 hs by studying the effect of the binder type (cement x hydratable alumina), the magnesia particle size (fine x coarse) and the additive package type. For this purpose, the binder and magnesia content was changed keeping their total amount fixed.

## EXPERIMENTAL PROCEDURE

The alumina-magnesia castable compositions selected for this investigation are listed in Table I. The top grain size was 8 mm. Microsilica at a level of 1% was added to enhance magnesia hydration resistance. All formulations were designed as a vibratable castable.

Two different binders were used: 70% calcium aluminate cement (C) and a hydratable alumina (HA).

Two magnesia sinter types with different grain size distribution were considered: magnesia under 75  $\mu\text{m}$  (M) and magnesia under 300  $\mu\text{m}$  (U). The amount of cement or hydratable alumina plus magnesia was kept at 12%.

Three additive package (I, II, and III) were compared in all compositions with cement-based formulations. For compositions with hydratable alumina, only additive package II was used.

Each composition was named by the binder content (C or HA) followed by the magnesia content, type and the additive package used. For example, the 6HA/6M-II composition has 6% hydratable alumina, 6% fine magnesia with additive package number II.

Table I. Castable compositions

	0C/12M	3C/9M	6C/6M	3HA/9M	6HA/6M
	0C/12U	3C/9U	6C/6U	3HA/9U	6HA/6U
Fused Al <sub>2</sub> O <sub>3</sub>	81	81	81	81	81
React. Al <sub>2</sub> O <sub>3</sub>	6	6	6	6	6
CAC	0	3	6	0	0
H A	0	0	0	3	6
M/U MgO	12	9	6	9	6
Microsilica	1	1	1	1	1
AP	0.25	0.25	0.25	0.25	0.25
	I, II, III	I, II, III	I, II, III	II	II

The flow decay of all compositions was measured in a vibratory table for 15 sec just after mixing and also after 30 min.

The cold crushing strength of the green samples (GCCS) were evaluated with the curing time (6, 12, 24, 72 and 168 hs) and they are the average of three samples.

The hydration test was carried out in an autoclave (T=152°C with 3 hs of soaking time) after curing. A hydration resistance index (HR) was established in order to rank the compositions regarding their slaking tendency. This index was measured in hours and it means that after that time there was no more damage by hydration. The Samples were evaluated by means of visual analysis, exaggerated permanent linear change (PLC), and a very low CCS.

Samples made by using only the matrix of the different compositions shown in Table II were also prepared in order to measure the exothermic profile. The solid to water ratio was adjusted to produce a paste.

Table II. Matrix compositions for exothermic profile.

	0C/12M	3C/9M	6C/6M	3HA/9M	6HA/6M
	0C/12U	3C/9U	6C/6U	3HA/9U	6HA/6U
React. Al <sub>2</sub> O <sub>3</sub>	32	32	32	32	32
CAC	0	16	32	0	0
H A	0	0	0	16	32
M/U MgO	64	48,0	32,0	48	32
Microsilica	4	4	4	4	4
AP	I, II, III	I, II, III	I, II, III	II	II

## RESULTS AND DISCUSSION

### Flow results

Considering the flowability of the compositions, immediately after mixing it's worth to mention that:

- AP-I required higher water content presenting a high initial flow independent to the magnesia particle size.
- AP-II tended to require a lower amount of casting water compared to the AP-I. The initial flow for the coarse magnesia was higher than the one with fine magnesia.
- AP-III appears to be the best one for the different levels of cement. In all cases, even with the lower percentage of water, the best flow was obtained with fine magnesia. AP-III, contrary to the other AP's, had some effect on the magnesia particles since there was a big difference of the flow for fine and the coarse magnesia. The flow for compositions with fine magnesia was higher than the one with coarse magnesia, in opposition to what it would be expected since fine magnesia particles disturb more the flow and setting behavior.

### Compositions with 12% magnesia

The results for the formulations without cement and 12% magnesia are presented in Table III. The GCCS for the fine magnesia compositions were very low (under 4.0 MPa) up to 24 hs of curing. After this time a sharp increase of the GCCS was observed. In the case of the coarse magnesia, no reasonable GCCS was observed even, after seven days of curing.

This kind of behavior was expected since the fine magnesia is more reactive than the coarse magnesia. The fine magnesia is probably reacting with silica and forming a MSH bond phase<sup>1</sup>. Because of the low specific surface area of the oxides used here (SSA fine magnesia ~ 1.5 m<sup>2</sup>/g), it's believed that hydrotalcite is not being formed as discussed elsewhere<sup>1,2</sup>. The results suggest that an even finer magnesia grain would develop a higher final GCCS in a shorter time. The exothermic profile did not show any peak until 72 hs which agrees with the low GCCS. Unfortunately, the exothermic profile test was interrupted before a possible increase of the GCCS development.

Table III. Green cold crushing strength evolution with time for 12% magnesia compositions.

	0C/12M-I	0C/12M-II	0C/12M-III
Water(%)	5.6	5.1	4.5
Flow 0'	160	130	190
Flow 30'	132	144	148
GCCS 6 h	1.5	1.1	1.4
GCCS 12 h	1.1	1.0	1.1
GCCS 24 h	1.5	2.3	3.5
GCCS 72 h	8.7	6.8	12.2
GCCS 168 h	20.0	15.6	23.6
HR (h)	≥ 24	≥ 24	> 168(?)
	0C/12U-I	0C/12U-II	0C/12U-III
Water(%)	5.4	4.8	4.4
Flow 0'	159	152	131
Flow 30'	133	118	112
GCCS 6 h	0.5	0.5	0.2
GCCS 12 h	0.7	0.5	0.4
GCCS 24 h	1.5	1.1	0.8
GCCS 72 h	2.7	3.1	2.3
GCCS 168 h	2.9	4.3	1.7
HR (h)	≥ 72	≥ 72	≥ 72

The additives tested here, developed for cement based compositions, did not affect the GCCS evolution as much as the magnesia particle size.

Compositions with 12% of fine magnesia were damaged by the hydration test up to 12 hs of curing. After 24 hs of curing, compositions with AP-I and AP-II did not show any damage by hydration. The formulation with AP-III and fine magnesia was damaged independently of the curing time. For compositions with coarse magnesia no damage was observed from 72 hs of curing. These results indicate that compositions with fine magnesia develop a faster hydration resistance than compositions with coarse magnesia.

### Compositions with 3% cement and 9% magnesia

The results for the formulations with 3% cement and 9% magnesia are presented in Table IV.

Table IV. Effect of the AP type on the castable properties with 3% cement and 9% magnesia.

	3C/9M-I	3C/9M-II	3C/9M-III
Water(%)	5.6	5.1	4.5
Flow 0'	176	133	189
Flow 30'	152	125	150
GCCS 6 h	5.4	2.9	2.9
GCCS 12 h	9.8	3.0	3.0
GCCS 24 h	18.4	5.3	11.6
GCCS 72 h	24.8	7.4	19.6
GCCS 168 h	31.5	11.8	28.8
HR (h)	≥ 12	≥ 12	≥ 12
	3C/9U-I	3C/9U-II	3C/9U-III
Water(%)	5.5	4.8	4.4
Flow 0'	165	148	144
Flow 30'	144	115	136
GCCS 6 h	0.7	0.9	0.5
GCCS 12 h	1.2	1.1	0.8
GCCS 24 h	6.7	3.7	1.8
GCCS 72 h	12.6	11.2	3.3
GCCS 168 h	18.0	12.0	7.6
HR (h)	≥ 24	≥ 72	≥ 24

Replacing 3% of fine magnesia by cement with AP-I and III promotes an earlier strength development followed by a higher GCCS after 7 days of curing. In the case of AP-II with 3% cement, the same behavior of the 12% magnesia was observed, i.e the GCCS, after 7 days, was smaller than the others. For the coarse magnesia, the addition of 3% of cement had a remarkable effect on the GCCS evolution for AP I and II and a smaller effect for AP-III.

Comparing the compositions with 3% cement, the AP-I promoted an earlier GCCS development for both, fine and coarse magnesia. Using fine magnesia a GCCS of 18 MPa was reached in 24 hs of curing while using coarse magnesia the same GCCS level was reached only after 7 days of curing. These results suggest that AP-I would be the best in terms of the strength development for both magnesia types (table IV). The AP-III with the fine magnesia started developing a reasonable strength after 24 hs and with the coarse magnesia, even after 7 days of curing the GCCS was the lowest among the compositions (7.6 MPa). The AP-II had similar behavior for both types of magnesia and a reasonable GCCS was achieved only after 3 days of curing. It seems that AP-II has less effect on GCCS development independent to the magnesia particle size, at least within 7 days of curing. Maybe, for longer curing time, it would be

possible to observe different behaviors depending on the magnesia particle size. These facts were in agreement with the temperature profile of the matrixes (figure 1). The strongest peaks for fine magnesia were observed with AP-I and AP-III. The AP-I developed a higher GCCS earlier than the AP-III. Therefore, in the exothermic profile, the peak for AP-I was formed first, and the peak for AP-III formed latter.

The GCCS for the compositions with 3% cement were not only dependent to the magnesia particle size but also had shown some dependence to the AP which emphasizes that a magnesia-cement-silica-additives interaction type might determine the behavior of the system.

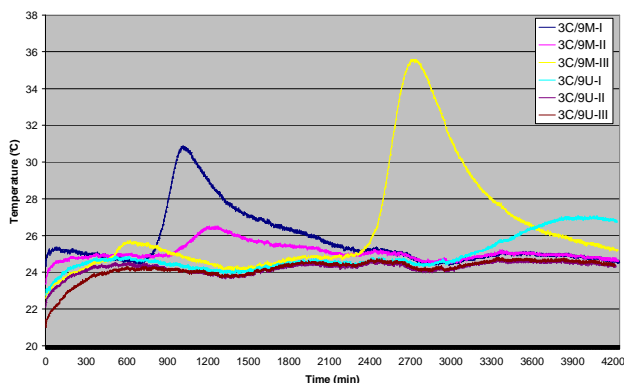


Fig. 1. Exothermic profile of matrix compositions based on castables with 3% cement and 9% magnesia.

Compositions with 3% cement were damaged by the hydration test up to 6 hs independently of the AP and magnesia size. With 12 hs of curing only compositions of coarse magnesia were damaged by the hydration test. For coarse magnesia no damage by hydration was observed after 24 hs (AP-I and III) and after 72 hs (AP-II). Again, compositions with fine magnesia have developed a higher hydration resistance in a shorter time.

### Compositions with 6% cement and 6% magnesia

The results for the formulations with 6% cement and 6% magnesia are presented in Table V.

The formulations with 6% cement presented earlier strength development and higher final GCCS when compared to the latter compositions, except when using AP-II. In this case the improvement observed was very small.

Compositions with fine and AP-I developed a reasonable resistance with 12 hs. The same system with AP-III reached the same level of resistance after 24 hs. In general, the GCCS was more dependent to the magnesia particle size than to the AP.

On the other hand, with AP-II, the magnesia particle size had minor importance, at least up to 7 days of curing. As mentioned before, it is expected that, for longer curing times, AP-II could be more sensitive to the magnesia particle size. AP-II seems to work as a stronger retarder of the cement hydration and, in order to notice, a higher GCCS would be necessary cure the compositions longer than 7 days or increase the curing temperature.

The effect of increasing the cement content from 3 to 6% can be easily noted on the exothermic profile, figure 2. For example, composition 6C/6M-I, compared to the composition 3C/9M-I, presented a higher peak temperature and positioned towards a shorter time. The same was

observed for the compositions with coarse magnesia and AP-I (6C/6U-I).

Table V. Effect of the AP type on the castable properties with 6% cement and 6% magnesia.

	6C/6M-I	6C/6M-II	6C/6M-III
Water(%)	5.7	5.2	4.5
Flow 0'	172	180	210
Flow 30'	145	166	160
GCCS 6 h	5.3	1.8	1.9
GCCS 12 h	19.8	3.4	2.8
GCCS 24 h	41.5	4.4	28.0
GCCS 72 h	55.0	11.7	45.9
GCCS 168 h	64.3	16.6	51.9
HR (h)	≥ 6	≥ 12	≥ 6
	6C/6U-I	6C/6U-II	6C/6U-III
Water(%)	5.5	4.8	4.4
Flow 0'	180	165	162
Flow 30'	142	130	127
GCCS 6 h	3.5	1.0	0.0
GCCS 12 h	4.7	0.9	0.7
GCCS 24 h	6.7	2.8	1.5
GCCS 72 h	19.0	8.4	15.3
GCCS 168 h	25.8	10.2	22.6
HR (h)	≥ 12	≥ 12	≥ 12

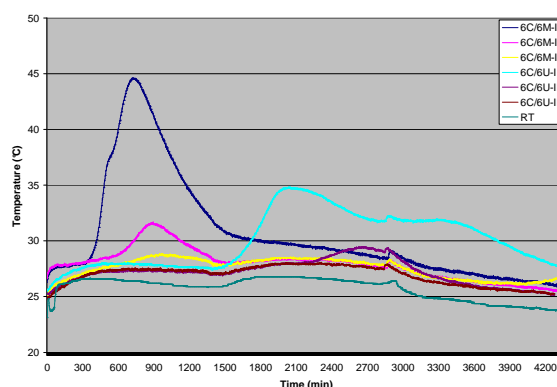


Fig. 2. Exothermic profile of matrix compositions based on castables with 6% CAC and 6% magnesia.

Regarding the autoclave test, in the first 6 hs all compositions with 6% cement were damaged, except for compositions 6C/6M-I and 6C/6M-III. Twelve hours of curing was enough to enhance the hydration resistance for the coarse magnesia compositions. Compared to the compositions with 0% and 3% cement, 6% cement promotes a faster hydration resistance development.

As observed elsewhere<sup>5</sup> and confirmed here, there was no direct relation between the GCCS and the slaking resistance of the compositions. Compositions with fine magnesia developed a fast slaking resistance compared to the one with coarse magnesia, in opposite to which would be expected. It's worth to mention that as microsilica content was fixed at 1%, the availability of microsilica for the coarse magnesia grains would be higher and, therefore, a higher slaking resistance for the coarse particles would be expected but this is not in agreement to the experimental results.

The GCCS increases with time and cement content as would be expected for AP-I and AP-III. For the first 24 hs the cement content followed by the additive type seems to be the most important variable in order to achieve a decent magnitude for the GCCS.

In the case of AP-II, during the whole curing time, the amount of cement and the magnesia particle size did not show a significant effect on the GCCS. Comparing the compositions with no cement and different additive packages there was no big difference of the final GCCS. However, introducing cement to the system, the final GCCS was strongly dependent on the AP. This result might be related to the stronger retarder effect of AP-II on the cement hydration.

### Compositions with Hydratable Alumina (HA)

The results for the formulations with hydratable alumina instead of cement with AP-II are presented in Table VI. The GCCS development for HA compared to the cement compositions with 3% and 6% of binder reveals an earlier evolution and a higher final GCCS for the HA system. As discussed by Ahari et al<sup>3</sup>, the presence of MgO appears to accelerate alumina hydration due to the formation of a hydroxalite-type hydrate. It's also known that magnesia accelerates the cement hydration<sup>3,4</sup>.

As the final GCCS was higher for the HA compositions than for the cement ones, this might suggest that magnesia has a stronger effect on the hydration of the HA and/or AP-II has a selective retarder effect on cement based compositions.

The final GCCS and the GCCS evolution were dependent to the HA content and to the magnesia particle size. The higher HA content with fine magnesia gave the highest final GCCS while the low HA content with coarse magnesia gave the lowest final GCCS. The exothermic profile for the HA compositions, figure 3, confirm this behavior. The strongest peak was the one for the composition 6A/6M and the weakest peak was for the composition 3A/9U.

Table VI. Compositions based on hydratable alumina and AP-II.

	3HA/9M-II	3HA/9U-II	6HA/6M-II	6HA/6U-II
Water(%)	6,0	5,0	6,1	5,5
Flow 0'	193	141	168	148
Flow 30'	163	117	145	134
GCCS 6 h	5.4	1.7	9.6	3.6
GCCS 12 h	6.8	1.7	11.2	3.8
GCCS 24 h	7.7	2.5	18.9	3.2
GCCS 72 h	16.1	11.1	32.3	21.8
GCCS 168 h	22.4	21.3	41.6	27.1
HR (h)	≥ 6	≥ 72	≥ 6	≥ 12

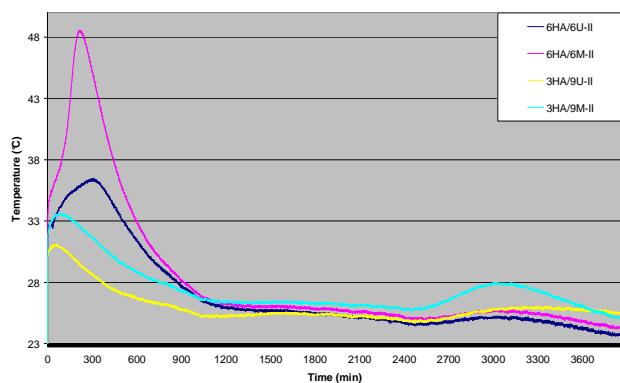


Fig. 3 Exothermic profile of matrix compositions based on HA system.

The hydration resistance of the compositions with fine magnesia was higher with HA than with cement. As observed with cement based compositions, increasing the binder content and using fine magnesia gives better HR index.

### CONCLUSIONS

The composition 6C/6M-I could be considered the best one in terms of GCCS evolution and hydration resistance. Curiously, the product based on this formulation was the worst in an industrial point of view, since a large number of pieces would present cracks after being dried. On the other hand, the product based on composition 6C/6U-II has presented a modest GCCS evolution and its mechanical resistance was lower than the 6C/6M-I composition. Despite of these properties the product based on this composition has been produced since 2006 and no cracks have been observed.

Parallel to the development of the system with cement and coarse magnesia, studies with hydratable alumina have been done in order to enhance GCCS and, at the same time, to keep the absence of cracks after drying. Tests have been initiated with formulation 6HA/6U-II with very good performance results at the customers and a free-crack production so far. The higher GCCS for the last composition has also avoided some handling problems observed for the 6C/6U-II in the first 24 hs.

In general, the hydration behavior was dependent to the curing time, additive package and magnesia particle size. It seems that when increasing the binder content, there was an increase of the slaking resistance for shorter curing times. However, for these compositions, increasing the cement or hydratable alumina content means a reduction of the magnesia amount which might explain part of this behavior.

Therefore, the crack phenomenon observed after drying the pieces appears not to be directly related to the GCCS and the hydration resistance, but might have other more important factors that is not being considered.

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