Comparison of Silica-sol and Low Cement Bonded Tabular Alumina and Spinel Castables

TIAN Zhongkai[1]*, LONG Bin[1], ZHOU Yunpeng[1], ZHANG Lanyin[1], KLAUS Sebastian[2], BUHR Andreas[2]

1 Qingdao Almatis Co. Ltd, 266071 Shandong, China
2 Almatis GmbH, 60528 Frankfurt, Germany
Corresponding author: Email: zhongkai.tian@almatis.com

Abstract
Silica-sol bonded castables have been in the market for many years. It is known that silica sol bonded castables are easier to dry when compared to low cement castables. For this reason silica sol bonded castables experienced a stronger focus especially in the recent years. Time is an important factor in refractory installations. Therefore, a fast heat up of monolithic linings is often desired by the refractory users.
This paper discusses the comparison between silica-sol bonded and low cement castables based on laboratory investigations. Three different kinds of silica-sol were tested in combination with three different matrix aluminas in a tabular alumina based test castable, and also in a spinel containing castable. The results show clear differences between sol and cement bonded castables, but also differences in castable behaviour for different sols. Also the matrix aluminas have a pronounced influence on the castable flow and strength properties, where especially the flow of sol bonded castables does not take advantage from reactive aluminas when compared to calcined alumina. The opposite applies for cement bonded castables.

1 Introduction
With the development of matrix aluminas the water demand for low cement castables (LCC) could be considerably decreased. Due to the low water content the castables decreased in porosity and gained in strength. Therefore, with regards to refractory applications such as slag infiltration or wear resistance low cement castable show better performance [1]. However, the high density makes the drying process more complex [2] and time consuming. Often advanced drying equipment is needed for LCC. Especially in winter times at curing temperatures below 10°C the risk of explosive spalling can be an issue [3, 4] (formation of hydrate phases CAH_{10} and AH_x-gel with high water content [5]).
To overcome long and complex drying procedures silica-sol bonded castables can be used in special applications [6, 7, 8]. However, the use of silica-sol bonded castables has advantages as well as disadvantages when compared to low cement castables:

- ✓ As there is no cement reaction present, curing is not needed.
- ✓ Faster dry-out, less risk of explosive spalling.
- ✓ High purity CaO free binder system, which leads to improved refractoriness and durability especially with silicate containing aggregates.

- ✗ The sol has to be delivered on side as a liquid suspension. This makes material handling more difficult.
- ✗ Freezing destroys the suspension and the sol has to be replaced. Especially in winter times, where silica-sol would have drying advantages, freezing might be an issue.
- ✗ Silica-sol bonded castables typically have a low cured strength of ~2 MPa. For large monolithic pieces this could result in crack formation.
- ✗ Silica-sol bonded castables are more sensitive to impurities, such as salts and therefore need special care in production
- ✗ Adjustments of working and setting time demand alternative approaches to LCC and are more complex [9].

Silica-sol bonded castables are CaO free which results in a higher refractoriness especially with alumino silicate aggregates. Due to the presence of silica, it is recommended to use CaO free aggregates and high purity matrix components, such as alumina [10] or spinel. For this reason, silica-sol bonded and low cement castables based on tabular alumina and spinel are discussed in this paper.

2 Experimental and Procedures
For investigations three different types of silica-sol products where used. Their main characteristics are shown in **Table 1**. The silica-sol H-40 with the highest SiO_2 content has a higher viscosity of 25 mPa·s.

Table 1 Main characteristics of silica-sol products used for investigations

Product name	H-25	H-30	H-40
SiO_2 [wt.-%]	25	30	40
Na_2O [wt.-%]	≤0.3	≤0.3	≤0.4
PH value	8.5	8.5	9
Viscosity (25°C) [mPa·s]	6	7	25

The investigated mixtures for the Tabular Alumina containing silica-sol bonded test castables are shown in **Table 2**. CT 9 FG is a calcined alumina produced by Almatis with a specific surface area of 0.8 m^2/g. Whereas, CL 370 (bi-modal, 3.0 m^2/g) and CTC 40 (multi-modal, 4.8 m^2/g) are reactive aluminas. A good rheology can be achieved by combination of matrix aluminas together with -45 MY and -20 MY Tabular Alumina T60/T64. The amount of silica-sol was chosen in order to obtain suitable initial flow properties.

For the spinel (MA-spinel) containing silica-sol bonded castables the amount of alumina was kept constant with variation in spinel fines (**Table 3**).

For each test series a cement bonded low cement test castable was chosen for comparison. Flow measurements after 10, 30 and 60 minutes were performed. Cold crushing strength and cold modulus of rupture were tested after curing, drying and firing. In addition, density and permanent linear change measurements were performed to complete the results.

Table 2: Investigated mixes of Tabular containing test castables

	[wt.-]	CT9FG/H25	CL370/H25	CTC40/H25	CT9FG/H30	CL370/H30	CTC40/H30	CT9FG/H40	CL370/H40	CTC40/H40	CL370/CAC
T60/T64	0.2 - 6 mm	60	60	60	60	60	60	60	60	60	60
	0 - 0.2 mm	15	15	15	15	15	15	15	15	15	15
	- 45 MY	5	5	5	5	5	5	5	5	5	
	- 20 MY	7	7	7	7	7	7	7	7	7	7
Alumina	CT 9 FG	13			13			13			
	CL 370		13			13			13		13
	CTC 40			13			13			13	
Cement	CA-14 M										5
SUM		100	100	100	100	100	100	100	100	100	100
Water	H_2O										4.4
Silica-sol	H-25	7.5	6	6.2							
	H-30				8.2	6.2	6.6				
	H-40							8.8	7	7.4	
Additives	ADS 3										0.3
	ADW 1										0.7

Table 3: Investigated mixes of Tabular and spinel containing test castables

	[wt.-]	90MY/H25	45MY/H25	20MY/H25	90MY/H30	45MY/H30	20MY/H30	90MY/H40	45MY/H40	20MY/H40	AR78/CAC
T60/T64	0.5 - 6 mm	56	56	56	56	56	56	56	56	56	55
Spinel AR 78	0 - 0.5 mm	16	16	16	16	16	16	16	16	16	15
	- 90 MY	15			15			15			
	- 45 MY		15			15			15		5
	- 20 MY			15			15			15	7
Alumina	CL 370	13	13	13	13	13	13	13	13	13	13
Cement	CA-14M										5
SUM		100	100	100	100	100	100	100	100	100	100
Water	H_2O										4.5
Silica-sol	H-25	6.2	8.2	8.6							
	H-30				6.4	8.9	9.2				
	H-40							7.2	9.7	10.4	
Additives	ADS 3										0.4
	ADW 1										0.6

3 Results and Discussion

3.1 Flow Properties of Castables

The vibrated flow values of the Tabular containing test castables are shown in **Fig. 1**. The CTC 40 containing mixes show the lowest flow for all silica-sol grades. The best flow was achieved with the calcined alumina CT 9 FG. Generally, an increase of silica-sol concentration results in lower flow values. The combination of CTC 40 and H-40, highest in SiO_2 concentration, results in no flow after 30 and 60 minutes.

The cement test castable shows very stable flow for a period of time of 60 minutes. These results underline the workability related sensitivity of silica-sol mixes. Wrong silica-sol concentration will quickly result in installation failures.

The flow values for the spinel containing test castables are shown in **Fig. 2**. Similar to the Tabular test castables, a higher concentration of silica-sol leads to lower flow values for the spinel containing castables. The flow values of the spinel containing test castables are strongly influenced by the spinel fineness. With the finest spinel (-20 MY) the flow values do not exceed 180 mm after 10 minutes.

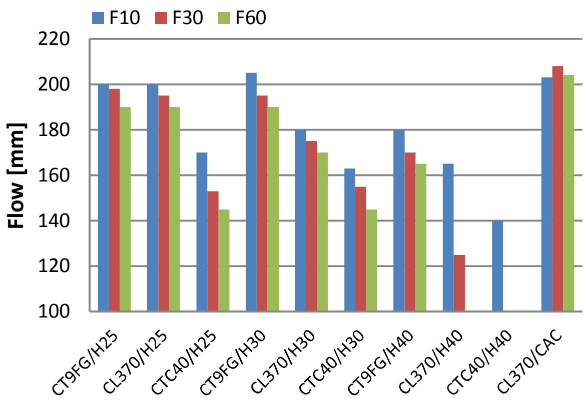

Fig. 1: Flow values of Tabular Alumina containing test castables after 10, 30 and 60 minutes

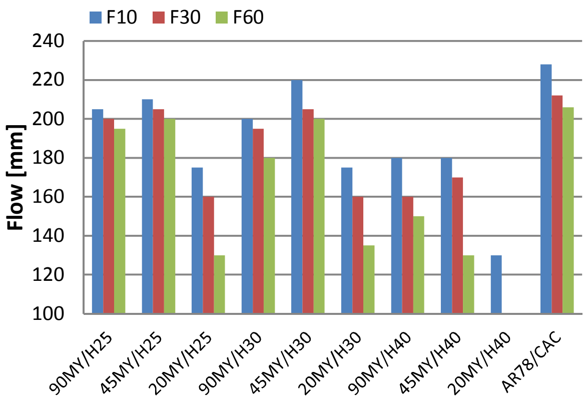

Fig. 2: Flow values of spinel containing test castables after 10, 30 and 60 minutes

The results show clearly that the flowability of a castable can be manipulated by a smart selection of fine matrix components.
It is remarkable that in any case coarser matrix components result in the best flow values. It is thinkable that the wetting and dispersing capacity of silica-sol is not sufficient for high surface matrix components. This may be due to the relative high viscosity of silica-sol products when compared to water in combination with dispersing agents.

3.2 Strength Investigations of Test Castables

The 20°C / 24h cured strength values for the Tabular containing test castables are shown in **Fig. 3**. The silica-sol based castables show all low CCS and CMoR when compared to the low cement bonded castable. Usage of CT 9 FG results in the lowest cured strength, independently from the silica-sol concentration.

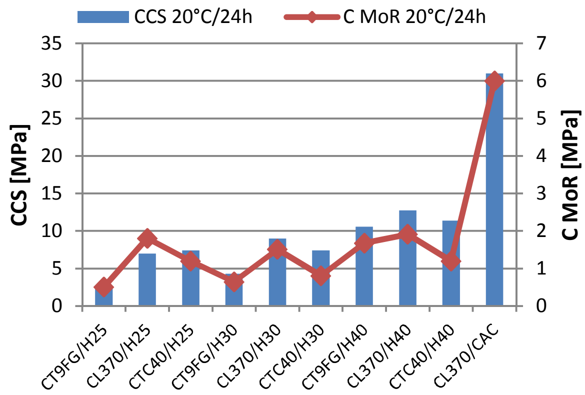

Fig. 3: Cured CCS and C MoR of Tabular containing test castables

In general, the cured strength increases with silica-sol concentration. All test castables based on the silica-sol H-40 show a CCS higher than 10 MPa. This is not surprising, as a higher amount of SiO_2 results in more effective silica-sol bonding (Si-O-Si network). The cement bonded test castable reaches the highest cured strength.

The investigations show that by choosing appropriate matrix components, such as CL 370, the cured strength of silica-sol bonded castables can be increased within a given silica-sol concentration.
The cured strength values for the spinel containing test castables were very comparable and are therefore not shown separately.

CCS results of the dried and fired Tabular containing test castables are shown in **Fig. 4**. The dried silica-sol samples have low strength when compared to the cement bonded castable.
The observed drop of strength at 1000°C is well known for cement based castables and is due to transition of calcium aluminate phases. All investigated silica-sol bonded castables do not show such a drop of strength values when fired at 1000°C. This is also the case for the spinel containing test castables as shown in **Fig. 5**. However, in contrast to the low cement castable, further strength increase between firing at 1000°C and 1500°C is minimal.
At firing temperatures of 1500°C the combination of a moderate silica-sol concentration (H-25 or H-30) together with CL 370 results in very good strength values with more than 150 MPa.
By far the highest strength values are obtained with the cement bonded test castable when fired at 1500°C.

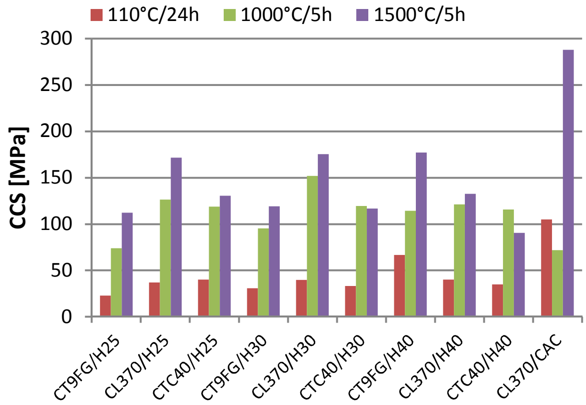

Fig. 4: Dried and fired CCS of Tabular containing test castables

With regards to the spinel containing silica-sol bonded test castables the highest values are obtained with –90 MY spinel as matrix component, independently from silica-sol concentration. The use of finer spinel results in lower strength values in any case. It is remarkable that for the silica-sol bonded spinel containing test castables, CCS is most pronounced when fired at 1000°C. In all cases the 1500°C CCS is lower when compared to the CCS at 1000°C, which is contrary to the strength results observed with the Tabular containing test castables. This drop in strength is due to sinter reactions which will occur between 1300°C and 1500°C in the ternary system Al_2O_3-MgO-SiO_2 [11].

Again, also with spinel, the cement bonded test castable shows the highest CCS when fired at 1500°C.

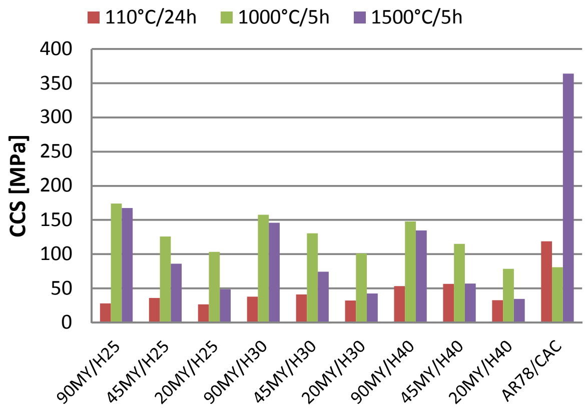

Fig. 5: Dried and fired CCS of spinel containing test castables

3.3 Density and Permanent Linear Change of Test Castables

The densities of the dried and fired Tabular containing test castables are shown in **Fig. 6**. Highest densification was observed with the reactive alumina CL 370. Here, already in a dried stage, the densities are with > 3.15 g/cm^3 clearly higher than for the other aluminas. The high densification levels with CL 370 are in accordance with the good strength results as presented in **Fig. 4**.

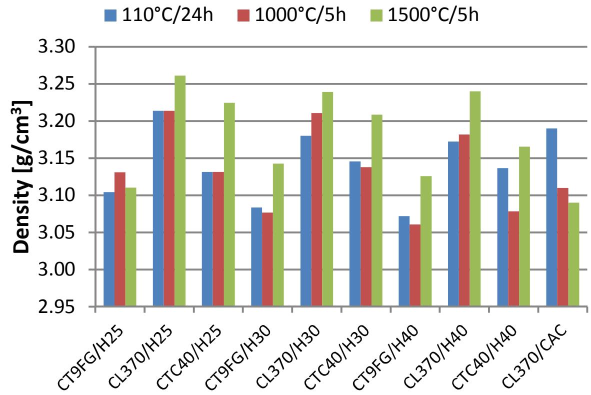

Fig. 6: Density measurements of dried and fired Tabular containing test castables

The drop of fired density for the cement bonded test castable is due to the transition reaction of the calcium aluminate phases. At 1650°C the castable reaches a density of 3.20 g/cm^3 (not shown in **Fig. 6**), which is in this case comparable with the densification levels of the 1500°C fired silica-sol bonded test castables.

The dried and fired permanent linear change (PLC) levels are shown in **Fig. 7**. After drying and firing at 1000°C no relevant linear change was observed. At 1500°C all silica-sol bonded test castables show clear shrinkage between -0.2% and -0.6%. Test castables with CT 9 FG are most affected by shrinkage. It is remarkable that the test castables with CT 9 FG show lowest densification, although PLC is most pronounced.

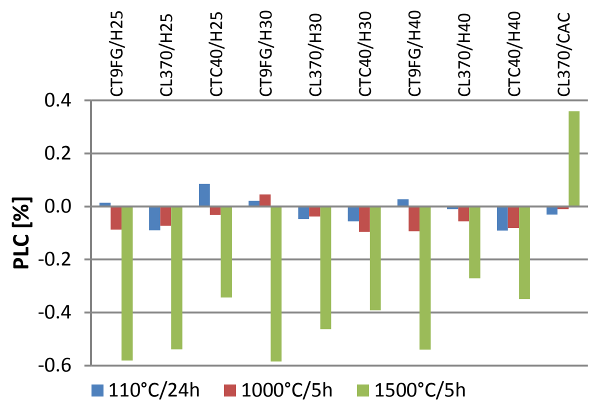

Fig. 7: Permanent linear change of dried and fired Tabular containing test castables

4 Conclusions

The results clearly show that an over-dosage of silica-sol results in worse flow properties. In addition, very fine matrix components with high specific surface will lead to decreased flow. It can be assumed that the wetting and deflocculating capabilities of the

investigated silica-sol products are not strong enough for those matrix components. On the other hand, it is shown that the strength properties of silica-sol bonded castables can be increased with reactive aluminas. Flow as well as strength properties can be adjusted and fine-tuned by alumina and spinel fines used as matrix components. It is shown that especially the reactive alumina CL 370 can be a good compromise between reasonable flow properties and strength.
In addition, all investigated silica-sol test castables exhibit very low cured strength, when compared to the cement bonded castable. Fired at 1000°C the strength is greatly increased. But at 1500°C the strength levels are comparable to the measured strength at 1000°C and do not increase much further. In all cases the 1500°C fired strength values are exceeded by the cement bonded test castable.

5 References

[1] R. Kockegey-Lorenz, A. Buhr, D. Zacherl, B. Long, S. Hayashi and J. Dutton, "Review of Matrix aluminas for refractory formulations," in *UNITECR 2011, Kyoto, Japan,* 2011: 2-B2-9

[2] D. Bell, "Development of a computer program to model drying of castable blocks and linings," *Refractories Applications and News, 2005,* 10(2): 18-22

[3] F. A. Cardoso, M. D. M. Innocentini, M. M. Akiyoshi and V. C. Pandolfelli, "Effect of curing time on the properties of CAC bonded refractory castables," *Journal of the European Ceramic Society,* 2004, 24(7): 2073-2078

[4] G. Palmer, J. Cobos, J. Millard and T. Howes, "The Accelerated Drying of Refractory Concrete - Part I: A Review of Current Unterstanding," *Refractories Worldforum,* 2014, 6(2): 75-83

[5] S. Klaus, J. Neubauer and F. Goetz-Neunhoeffer, "Hydration kinetics of CA_2 and CA - Investigations performed on a synthetic calcium aluminate cement," *Cement and Concrete Research,* 2013, 43: 62-69

[6] B. Myhre and H. Fan, "Gel bonded castables based on microsilica as binder," in *UNITECR 2011, Kyoto, Japan*, 2011.

[7] A. K. Singh and R. Sarkar, "Effect of Binders and Distribution Coefficient on the Properties of High Alumina Castables," *Journal of the Australian Ceramics Society Volume,* 2014, 50(2): 93-98

[8] K. H. Dott, "Experiences with Oxycarbide Products in CAS-OB bells and lances," in *3rd International Conference on Refractories, Jamshedpur, India,* 2013: 87-92

[9] M. V. M. Magliano, E. Prestes, J. Medeiros, J. L. B. C. Veiga and V. C. Pandolfelli, "Colloidal silica selection for nanobonded refractory castables," *Refractories Applications and News,* 2010, 15(3): 14-17

[10] M. Hochegger, M. Blajs, B. Nonnen and P. Zottler, "First Practical Results With COMPAC SOL A100S-15 - A High-End Sol-Bonded Castable Designed for EAF Deltas," *RHI worldwide,* 2013, 1: 14-19

[11] B. Sandberg, B. Myhre and J. L. Holm, "Castables in the system $MgO-Al_2O_3-SiO_2$," in *UNITECR 1995, Kyoto, Japan,* 1995: 19-22