MATERIAŁY CERAMICZNE /CERAMIC MATERIALS/, 61, 4, (2009), 228-232

www.ptcer.pl/mccm

Secar 41 – a new calcium aluminate cement for regular and insulating castables

C. Wöhrmeyer, C. Parr, P. Gudovskikh

KERNEOS S.A., Paris
e-mail: christoph.wohrmeyer@kerneos.com; www.secar.net

Streszczenie

Regular and insulating castables for application temperatures of 1000°C to 1500°C are often formulated with calcium aluminate cements containing either 40% Al_2O_3, for example Ciment Fondu® (CF), or 50% Al_2O_3 as Secar®51 (S51). While CF is frequently used in insulating concretes together with vermiculite or perlite, S51 is often the preferred choice for dense regular castables with good fluidity and high abrasion resistance. It exhibits also excellent dry-gunning properties. S51 has a low water demand and gives high strength due to its mineralogical composition. It allows application of temperatures up to 1500°C when aggregates with an adequate temperature resistance are used. CF focuses more on the lower temperature application and offers a very good usage value for very cement rich mixes like insulating castables based on vermiculite, perlite and lightweight fireclay.

This paper will discuss the introduction of Secar®41 (S41) into the family of Secar® calcium aluminates in Europe. Secar®41, a fused calcium aluminate cement with 46% Al_2O_3, already successfully used in the American refractory industry for many years, combines the low water demand of Secar®51 with a superior refractoriness compared to CF. It allows improving the rheology and temperature resistance compared to CF-based lightweight and dense castables. Where S51 was chosen for its superior flow property and abrasion resistance compared to CF, S41 offers an excellent alternative with an adapted cost/performance-ratio. Compared to CF, S41 gives for example a 30-40°C higher application temperature when combined with fireclay. This brings more furnace security in case that overheating occurs unexpectedly. Due to the optimised mineralogy of S41, it exhibits a higher hydraulic potential than CF. Secar®41 has the potential to improve insulating castables either by increased strength at constant density or by better insulating properties through density reduction without compromising the strength level. These unique properties of Secar®41 make it an all-round hydraulic binder for dense and insulating castables with application temperature of 1350°C, which shall be installed either by vibro-casting, dry-gunning or traditional rodding methods.

Keywords: Castable, Aluminate, Cement, Refractories, Mechanical properties

SECAR 41 – NOWY CEMENT GLINOWY DO BETONÓW ZWYKŁYCH I IZOLACYJNYCH

Betony zwykłe i izolacyjne do temperatur stosowania wynoszących od 1000°C do 1500°C są często przygotowywane z cementów glinowych zawierających albo 40% Al_2O_3, np. Ciment Fondu® (CF), lub 50% Al_2O_3 w postaci cementu Secar®51 (S51). Podczas gdy CF wykorzystywany jest często w betonach izolacyjnych razem z wermikulitem lub perlitem, S51 jest często preferowanym wyborem w przypadku gęstych, zwykłych betonów o dobrej płynności i wysokiej odporności na ścieranie. Wykazuje on również doskonałe właściwości podczas torkretowania na sucho. S51 ma niskie zapotrzebowanie na wodę i daje wysoką wytrzymałość wynikającą z jego składu mineralogicznego. Pozwala na zastosowanie w temperaturach do 1500°C wtedy, gdy użyte są kruszywa o odpowiedniej odporności temperaturowej. CF ogniskuje się bardziej na niższej temperaturze stosowania i oferuje bardzo dobre właściwości użytkowe w przypadku mieszanin bardzo bogatych w cement, takich jak betony izolacyjne bazujące na wermikulicie, perlicie i lekkich glinach ogniotrwałych.

W artykule tym dyskutowane będzie wprowadzenie cementu Secar®41 (S41) do rodziny glinianów wapnia Secar® w Europie. Secar®41, topiony cement glinowy zawierający 46% Al_2O_3, stosowany z powodzeniem już od wielu lat w amerykańskim przemyśle materiałów ogniotrwałych, łączy niskie zapotrzebowanie na wodę cementu Secar®51 z doskonałą ogniotrwałością w porównaniu z CF. Pozwala on na poprawienie reologii i odporności temperaturowej w porównaniu z betonami lekkimi i gęstymi bazującymi na CF. Tam gdzie S51 był wybrany z powodu lepszego płynięcia i odporności na ścierania w porównaniu z CF, S41 oferuje doskonałą alternatywę o obranym stosunku koszt/jakość. W porównaniu z CF, S41 daje na przykład o 30-40°C wyższe temperatury stosowania przy połączeniu z gliną ogniotrwałą. Przynosi to zwiększenie bezpieczeństwa dla pieca w przypadku wystąpienia nieoczekiwanego przegrzania. W związku ze zoptymalizowaną mineralogią, S41 wykazuje wyższy potencjał hydrauliczny niż CF. Secar®41 ma potencjał polepszenia betonów izolacyjnych albo poprzez zwiększoną wytrzymałość przy stałej gęstości, albo poprzez lepsze właściwości izolacyjne w związku z redukcją gęstości bez kompromisowego zmniejszenia poziomu wytrzymałości. Te unikalne właściwości cementu Secar®41 czynią go uniwersalnym spoiwem hydraulicznym w przypadku betonów gęstych i izolacyjnych o temperaturze stosowania wynoszącej 1350°C, które mogą być instalowane metodami odlewania wibracyjnego, torkretowania na sucho lub tradycyjnego sztychowania.

Słowa kluczowe: beton ogniotrwały, glinian, cement, materiały ogniotrwałe, właściwości mechaniczne

Introduction

Since calcium aluminate cement (CAC) is a major component of regular dense and especially insulating castables, it plays a major role for the usage value of these monolithic refractories. Secar®41 was introduced to the North American market some years ago in response to the refractory industry requirement for a low range calcium aluminate cement with a lower iron content than Ciment Fondu®. This cement, containing 7% iron oxide, has also found applications in the civil and construction chemistry industry due to its more fluid rheology and longer open times as compared to Ciment Fondu®, while still retaining the very rapid hardening properties known to calcium aluminate cements.

In the European monolithic refractories market mainly 40% Al_2O_3 containing CAC with about 15% Fe_2O_3 like Ciment Fondu® (CF) and low iron containing 50% Al_2O_3 containing CAC with ca. 2% Fe_2O_3 like Secar®51 (S51) have been used so far in regular castables together with fireclay or insulating natural aggregates since many years. But the experiences from the American refractory market with the 46% Al_2O_3 containing cement Secar®41 (S41) have confirmed that cost/performance-optimisation is achievable for the mid temperature range regular castables when all 3 cements: CF, S41, and S51 are available and their usage values are fully exploited in the different castable systems. Examples for application properties will be shown in the following. A dense fireclay castable and an insulating mix based on vermiculite have been chosen as model systems to demonstrate the different effects achievable by the 3 CAC.

Calcium aluminate cement characteristics

S41 is, from chemical point of view, an intermediate calcium aluminate cement between S51 and CF. While CaO and SiO_2 contents are almost on the same level for all three cements, the main difference is coming from the Al_2O_3/Fe_2O_3 ratio. S41 contains about 46% Al_2O_3 and 7% Fe_2O_3. CF has 40% Al_2O_3 only, compensated by a higher Fe_2O_3 content of about 15%, while S51 is more pure with its 51% Al_2O_3 and only 2% Fe_2O_3. All chemical components (Fig. 1) are combined in mineralogical multi-oxide phases. Therein the calcium mono-aluminate plays the most prominent role due to its hydraulic potential. In all three of these CAC, the $CaAl_2O_4$-phase is present as the major phase with a content of more than 50%.

The 3 cements are made by grinding of pure fused clinker to a specific surface area (Blaine) of 4000 cm²/g for S51, 3400 cm²/g for S41 and 3000 cm²/g for CF. With its physical, chemical and mineralogical composition S41 reaches almost the same high hydraulic potential and low water demand as S51, and both superior to CF. That brings castable rheology, binding properties, and strength level of S41 almost up to the level of S51 and allows higher temperature resistance compared to CF. Using the pyrometric cone method on neat cement pasts, the temperature resistance of S41 has been found 35°C higher than of CF, which gives security to above than 1300°C (Fig. 2). The iron oxide content of 7% is the only limitation for S41 compared to S51 with respect to temperature resistance and performance in reducing atmospheres, fields, where S51 shows superior performance.

Castable test methods

Castable test methods like flow under vibration, and physical properties as bulk density, permanent linear changes and strength have been determined. Samples have been prepared by casting into moulds under vibration in case of the dense castable and slightly rodding in case of the vermiculite mix, which has been adjusted to an almost self flowing consistency. After curing at 20°C and >90% relative humidity during 24h samples have been dried at 110°C for another 24h before they have been fired with holding times of 6h at the specified temperatures. Furthermore, the castable hardening process has been followed by the ultrasonic method as described in Ref. [1]. The CAC hydration process has also been analysed by registering the temperature evolution over time as described in Ref. [2]. The following model recipes have been chosen to study the characteristics of the 3 different CAC.

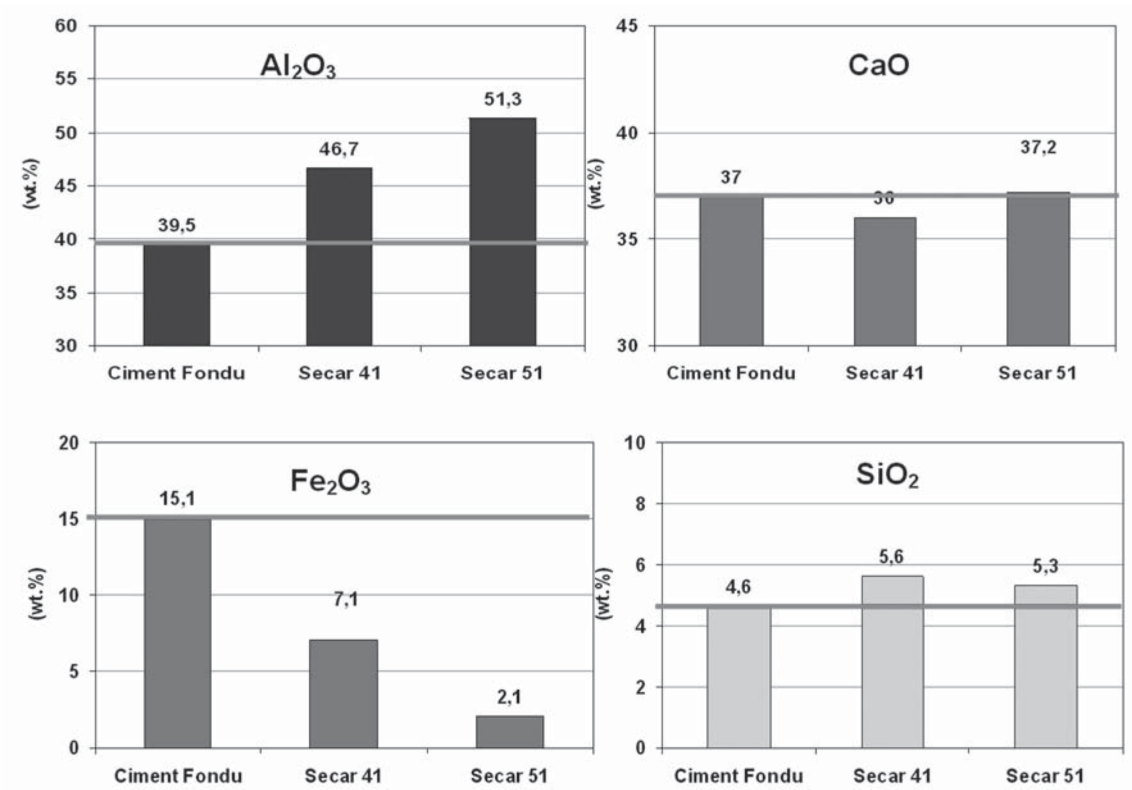

Fig. 1. Chemistry of Ciment Fondu®, Secar®41 and Secar®51.
Rys. 1. Skład chemiczny cementów Ciment Fondu®, Secar®41 and Secar®51.

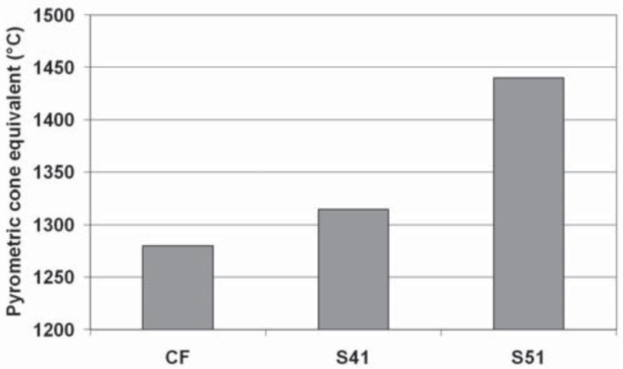

Fig. 2. PCE of 3 calcium aluminate cements (neat paste).
Rys. 2. PCE 3. cementów glinowych (pasta bez domieszek).

Table 1. Lightweight (LW) and dense castable (DC) model recipes.
Tabela 1. Modelowe receptury betonów lekkich (LW) i gęstych (DC).

	Lightweight (LW) castable			Dense castable (DC)		
	LW-CF	LW-S41	LW-S51	DC-CF	DC-S41	DC-S51
Vermiculite 0-2 mm	30	30	30			
Plastic clay	10	10	10			
Fireclay 0-6 mm				75	75	75
CAC CF	60			25		
CAC S41		60			25	
CAC S51			60			25
H_2O	125	120	125	9	8 or 9	9

A lightweight castable (LW) is based on pre-expanded vermiculite and uses 60% by weight of CAC. Mixed with 120-125 mass % water and installed by casting without any vibration, only little rodding, it results typically in a castable bulk density of ca. 500-600 kg/m^3 after drying at 110°C. The dense castable (DC) uses Mulcoa®47 as aggregate and 25 mass % CAC as binder. Water addition has been adjusted here in a first series to 9% for all CAC and also to 8% in case of Secar®41, which brings it to the same initial fluidity as Ciment Fondu® with 9% water. Bulk densities of typically 2350 kg/m^3 have been achieved here after drying.

Test results

Dense castable

Compared to CF lower water demand has been achieved with S41 and S51. Mixed with 9% water the dense fireclay castable shows significantly higher initial flow values with S41 and S51 than with CF. DC-S41 mixed with only 8% water exhibits equal flow as DC-CF with 9% water (Fig. 3). Flow decays already during the first 30 minutes for CF, while S41 and S51 create a more stable flow during this period (Fig. 4), which gives enough time to install the castable properly. With S51 and S41, a longer open time can be achieved before they start to set, which gives more flexibility during installation of the S41 and S51 based products since unforeseen interruptions, for example due to machine problems or other technical aspects, may happen at the job side. CF is progressively losing its fluidity right after castable mixing, which makes casting installation of dense concretes more complicated since vibration time should be adapted to the changing fluidity of the castable in order to achieve constant degree of compaction during the installation period.

The castable stiffening and hardening period has been studied with the ultrasonic method. The strong velocity increase of the ultrasonic signal, which passes through the sample, indicates the stiffening of the castable to a level, where it loses completely its fluidity. This is the case after 180 minutes for CF, 200 minutes for S51 and 280 minutes in case of S41 (Fig. 5). Soon after stiffening, the massive cement hydration starts as can be observed by the exothermic heat development in the castables, which brings their temperatures up to 42 to 47°C (Fig. 6). In all cases, the massive hydration is completed after less than 10 hours so that de-moulding can be started without problems. CF stiffens quite quickly due to its minor phase content, which also trigger the massive precipitation of hydrates, and rapid gain in strength.

Figure 7 summarises the strength, bulk density and permanent linear change of the tested mixes. The initial vibration flow value as a function of cement type and water addition is also indicated in Fig. 7 to put the physical properties into relation with the castable rheology achieved with the different cements and water additions. If water addition is kept constant at 9%, strengths are almost equal for CF and S41 after firing at 800°C, while after 1100°C firing, S41 shows its advantage. S51 gives superior strength after firing both at 800°C and 1100°C.

With the initial flow adapted to the same level as for CF by reducing water from 9 to 8%, a significant strength increase was observed with S41 for both test temperatures. For 800°C, strength increased by 24%, and for 1100°C even by 43%, which brings the mix with S41 at 8% water to the level of S51 with 9% water. Bulk density remained at the same level for all mixes with 9% water, and increased only marginally by 2% for S41 with 8% water due to the lower porosity as a consequence of the reduced amount of mixing water. At 9% water, S41 is the cement, which creates the lowest shrinkage after firing compared to the dried prisms. The water reduction from 9% to 8% for S41 further reduced the shrinkage at 1100°C. This tendency becomes even more dominant after heating at 1350°C, where CF shows the biggest shrinkage followed by S41 (9% H_2O), while S41 at 8% H_2O and S51 remain almost stable (Fig. 8).

The ratio between cold crushing strength (CCS) and cold modulus of rupture (CMOR) increases significantly for DC-CF after heating to 1350°C compared to the other mixes (Fig. 9).

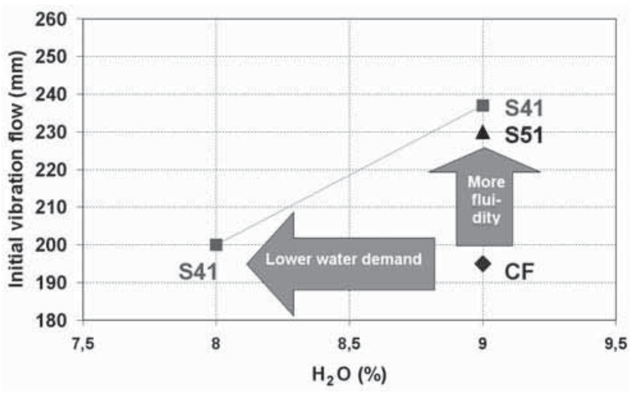

Fig. 3. Initial vibration flow of dense fireclay castable with CF, S41 and S51 at 9% mixing water and also for S41 at 8% mixing water.
Rys. 3. Początkowy przepływ wibracyjny gęstego betonu zawierającego glinę ogniotrwałą i cementy CF, S41 lub S51 oraz 9% wody zarobowej, oraz betonu z cementem S41 i 8% wody zarobowej.

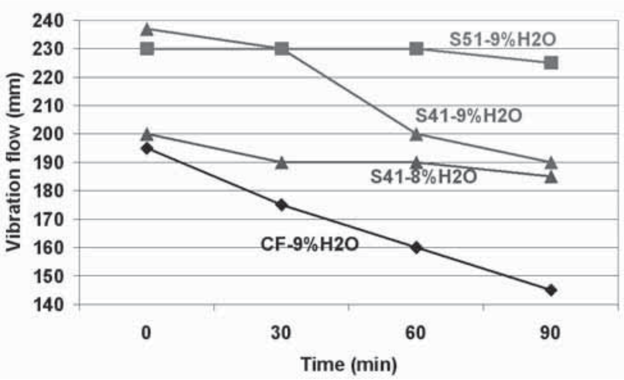

Fig. 4. Flow profile of dense fireclay castable with different CAC and amount of mixing water.
Rys. 4. Profil przepływu gęstego betonu zawierającego glinę ogniotrwałą oraz różne CAC i ilości wody zarobowej.

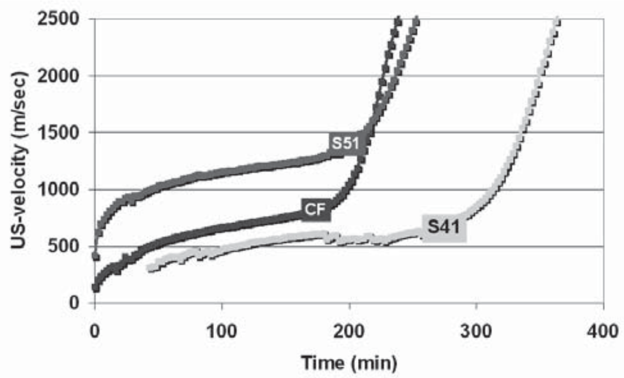

Fig. 5. Ultrasonic profile of dense castable with 3 different CAC, 9% H_2O.
Rys. 5. Profil ultradźwiękowy betonu gęstego z 3. różnymi CAC, przy 9% H_2O.

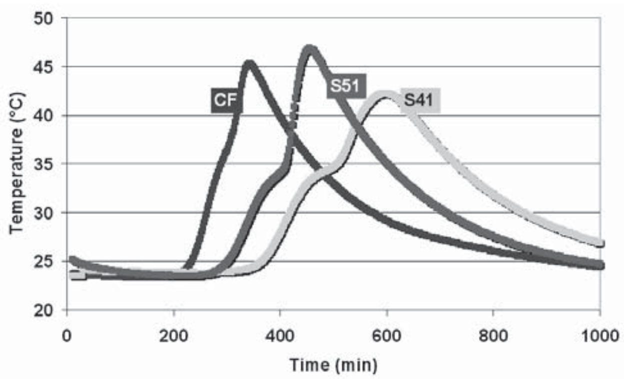

Fig. 6. Exothermic profile of dense castable with 3 different CAC, 9% H_2O.
Rys. 6. Profil egzotermiczny betonu gęstego z 3. różnymi CAC, przy 9% H_2O

This indicates that some liquid might have occurred already at this temperature in case of CF, which has modified the microstructure. Since this liquid solidifies during cooling of the sample, the measured CCS is here not representative anymore for the performance of the CF-based castable, and can't be taken into account to qualify that mix. The castables based on S41 and S51 show still normal behaviour with little or no liquid formation at 1350°C.

Lightweight castable

The lightweight concretes have been mixed after adding 125 wt% of water to the dry mix (LW-S51 and LW-CF). LW-S41 was mixed with 120% water only since the mix was already very liquid with 125% and bleeding started to occur. After about 3 to 4 hours, all castables start to set, and cement hydration brings the castable temperature up to 47°C for CF, while S41 and S51 remain at 32-33°C. The peak occurs after 5 to 6 hrs in all cases (Fig. 10). Since in case of CF the temperature raises higher, the cement hydrates might have been converted already in this case from CAH10 and C2AH8 into C3AH6 and AH3 [3]. Furthermore, the higher temperature bears the risk that water might evaporate too quickly from the concrete structure on the job side, while during the lab test, the samples have been cured at >90% humidity to limit this risk. If too much water would evaporate, not enough would remain available in the concrete for a complete cement hydration and optimal strength formation.

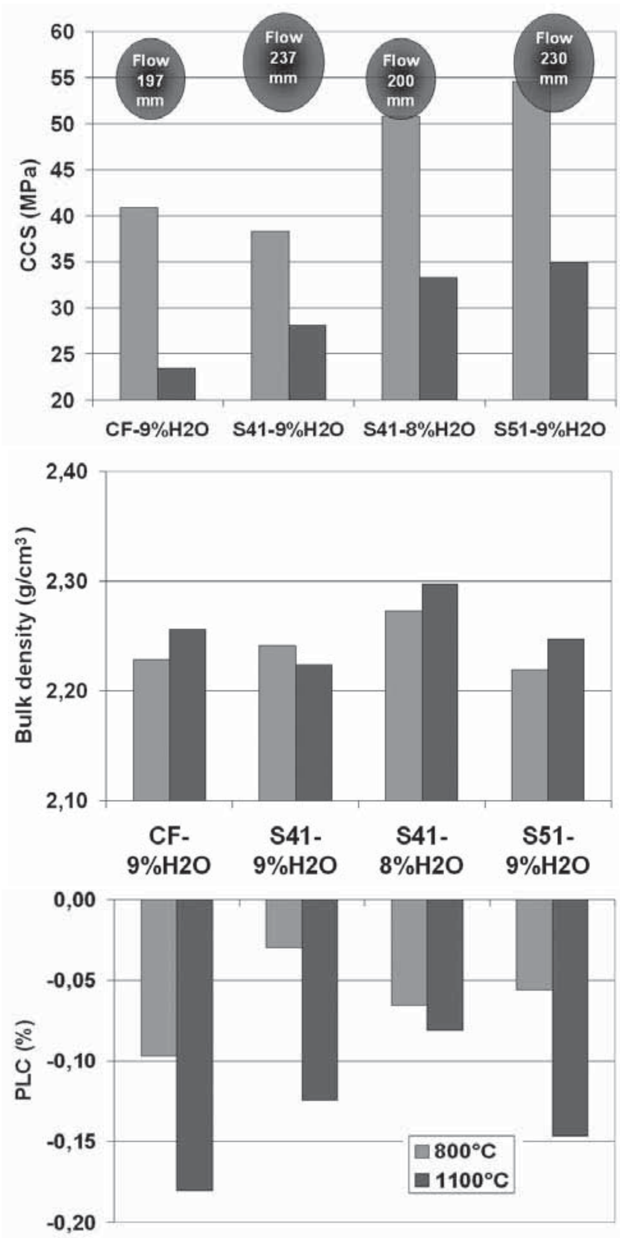

Fig. 7. Cold crushing strength, bulk density, and permanent linear change of dense fireclay castable with 3 different CAC after pre-firing at 800°C and 1100°C. S41 tested with 9% and 8% mixing water.
Rys. 7. Wytrzymałość na ściskanie w temperaturze pokojowej, gęstość pozorna i trwała, liniowa zmiana wymiarów gęstego betonu zawierającego glinę ogniotrwałą z 3. różnymi CAC po wstępnym wypaleniu w 800°C i 1100°C. S41 badano z 9% i 8% wody zarobowej.

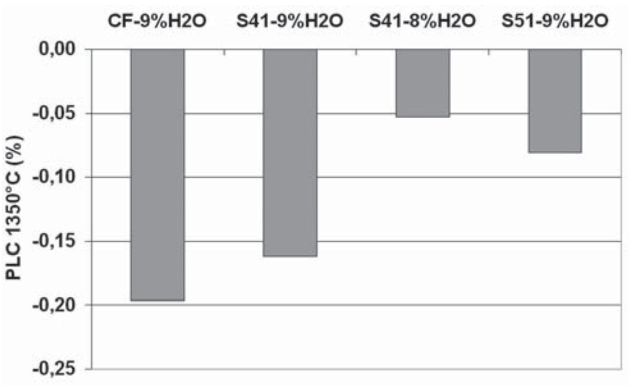

Fig. 8. Permanent linear change after heating at 1350°C for dense castable.
Rys. 8. Trwała liniowa zmiana wymiarów po wygrzaniu w 1350°C w przypadku betonu gęstego.

The bulk densities of the 3 lightweight mixes are in the range of 560 to 590 kg/m^3 after drying at 110°C with the lowest for S51 and the highest for CF. Contrary to the bulk density, the strength was found at the highest level for S51 with S41 being intermediate. The lowest strength was measured for CF despite the slightly higher density. Here the mineralogy and the hydraulic power of the different CAC with their specific hydration paths play a more important role than purely the density.

Summary and conclusion

Secar®41, which has an intermediate chemistry between Ciment Fondu® on one hand and Secar®51 on the other, offers a rheological performance and a hydraulic potential, which is much closer to S51 than to CF. The temperature resistance of Secar®41 is about 35°C superior to Ciment Fondu®. This is achieved by an increased Al_2O_3 and a reduced Fe_2O_3 content compared to CF. Applied in a dense fireclay concrete, Secar®41 offers more flexibility during castable installation with its stable rheology and an open time similar to Secar®51. Compared to CF it also gives a higher fluidity at equal water addition. Reducing the mixing water to a level, where equal initial flow for S41 and CF is achieved, a significant higher strength was observed with S41 compared to CF. With these properties Secar®41 reaches almost the same performance as Secar®51, which is also known for its excellent gunning behaviour. However, Secar®51 is the preferred cement when temperatures are relatively high and lower iron oxide content is required for more reducing furnace atmospheres. Applied in vermiculte lightweight castables, the hydraulic behaviour of Secar®41 is once again almost identical to Secar®51, and strength is significantly higher than with Ciment Fondu®. Nevertheless the strength of S41 in this system is intermediate between CF and S51. All together Secar®41 is an excellent all-round calcium aluminate cement for medium temperature application. It combines the stable rheological features from Secar®51 with an increased temperature resistance and a lower iron oxide content compared to Ciment Fondu®. Secar®41, together with Ciment Fondu® and Secar®51, help refractory castable formulators to optimise the cost/performance ratio in all segments of regular castables as the experience from the North American market has shown already. This advantage can now also be exploited by the refractory market in Europe and beyond.

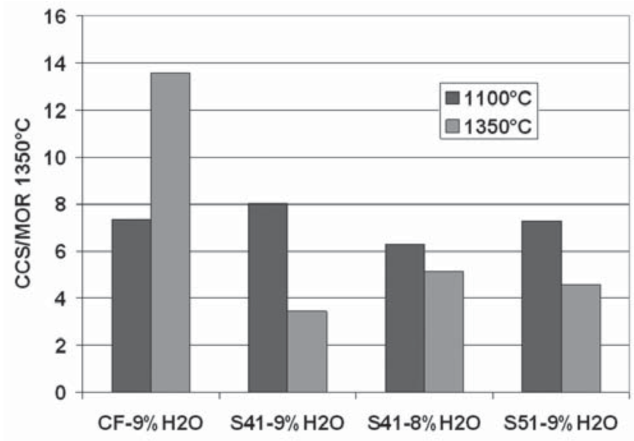

Fig. 9. Ratio between CCS and CMOR after heating at 1100°C and 1350°C for dense castable.
Rys. 9. Stosunek CCS i CMOR po wygrzaniu w 1100°C i 1350°C w przypadku betonu gęstego.

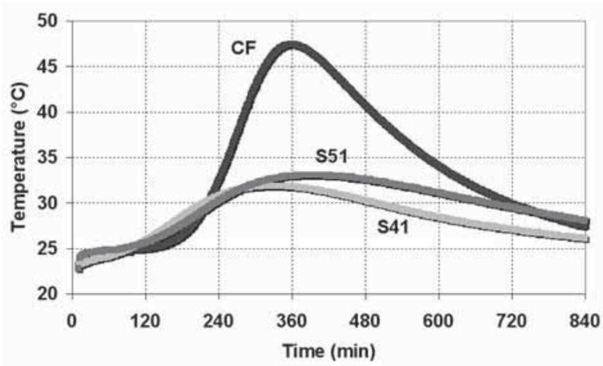

Fig. 10. Exothermic heat profile of vermiculite lightweight castable.
Rys. 10. Egzotermiczny profil termiczny lekkiego betonu wermikulitowego.

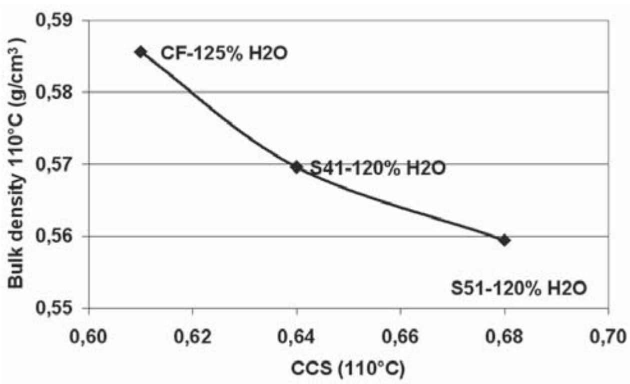

Fig. 11. Bulk density and cold crushing strength of vermiculite lightweight castable after drying at 110°C.
Rys. 11. Gęstość pozorna i wytrzymałość na ściskanie lekkiego betonu wermikulitowego po wysuszeniu w 110°C.

References

[1] Simonin F., Wöhrmeyer C., Parr C.: "A new method for assessing calcium aluminate cements", UNITECR'05 conference proceedings, Smith J.D. (Ed.), American Ceramic Society, Orlando, USA, 2006, pp. 849-853.
[2] Alt C., Wong L., Parr C.: "Measuring castable rheology by exothermic profile", UNITECR'01 conference proceedings, Cancun, Mexico, 2001, pp. 1517-22.
[3] Fryda H., Charpentier E., Bertino J.M.: "Accelerated test for conversion of calcium aluminate cement concrete", in Calcium Aluminate Cements: Proceedings of the Centenary Conference, Avignon, France, 2008, p. 159-169.

♦