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Refractory concretes bonded with calcium aluminate phosphate (CAP) mechano-chemical binder

Introduction

Binder is the main ingredient in all refractory concretes contributing to the strength development during the initial curing periods and installation of refractory-concrete linings.

Conventional refractory cements (calcium aluminate, high Al_2O_3 , aluminate phosphate and other) continue to be the most popular hydraulically setting binders used for bonding refractory concretes. However, refractory concretes bonded with traditional binders have limited refractory applications because of the strength degradation resulting from structural defects caused by occurrence of dehydration process, bonds disruption, easy-melting compositions forming. Unlike calcium aluminate (CA) cements, calcium aluminate phosphate (CAP) mechano-chemical binder (specially formulated, suspension-aggregate mix) retains its integrity when subjected to prolonged periods of high heat, cyclic heating and cooling, and other deleterious conditions of corrosion and erosion presented in high temperature industrial processes. It has a sequential effect on the service life and performance of a refractory-concrete lining bonded with CAP mechano-chemical binder; that is, 1) quick installation of refractory lining and low construction costs, 2) developing of initial strength requires fewer times, 3) thermal efficiency permitting thinner lining.

Economics demand rapid relining of processing units. Developing of initial strength during a heatup of the refractory lining within 8-10 h for CAP mechano-chemical binder, in contrast to 24 h after placement for high Al_2O_3 cements and 28 days for normal Portland-cement, could become commonplace prior to final heatup of the units being installed with using of high concentrated bonding suspensions (HCBS) technology.

Experimental program

The dense refractory concretes compositions developing is critically dependent on requirement of the minimum porosity and shrinkage to assure volume stability. It is important also that the voids between the grains of aggregate and binder to be filled to achieve the proper placeability and workability of concrete mix.

Among various refractory aggregates that might be considered for evaluating the bonding characteristics of all CAP binders types only fused and sintered aluminas (corundum) have adequate refractoriness and are sufficiently chemically inert. Properties of aggregates that markedly affect setting properties are soluble salts, colloidal fines, particle-size distribution, amount of porosity and pore size [1]. Except for the larger amount of open porosity in the coarser fused alumina grain, both aggregates can be sufficiently controlled to have no effect on setting time.

Evaluation of CAP binders in concrete compositions requires that the variation in particle size of aggregate be minimized. This can be achieved by using closed aggregate sizes to approximate the ideal continuous size distribution designed for maximum packing [2]. The ideal distribution will be matched at one less than the number of size fractions used. It follows then that the ideal distribution will be more closely matched as the number of sized components increases.

Maximum packing is accomplished for the two-fraction aggregates mixes when they contain 60-70% coarse and 30-40% small fraction [3]. Wherein, the dense packing can be accomplished when the average size of small aggregate is 6-7 times less than the coarse. According to Andreas [3], the condition for the dense packing of aggregate in concretes is the following:

$$Y_i = 100 \cdot \sqrt{\frac{d_i}{D}}$$

Where Y_i – fraction amount with size d_i , %; D – the larger fraction of mix size, mm; d_i – any given fraction size, mm.

Considering this, the dense packing for aggregate mix with maximum grain size 3 mm is obtained when it contains 60% of 3-0,5 mm fraction and 40% of less than 0,5 mm fraction. For aggregate mix with maximum grain size 2 mm the dense packing is obtained when it contains 50% of 3-0,5 mm fraction and 50% of less than 0,5 mm fraction.

Since CAP mechano-chemical binder with 0,05 mm maximum particle size is used for corundum refractory concretes bonding [4], previously completed calculations allowed to use the aggregate containing 60% of 3-0,5 mm fraction and 40% of less than 0,5 mm fraction for further evaluation of concrete compositions. It is imperative, therefore, that the “aggregate-binder” optimal ratio for CAP concrete compositions corresponds with the following requirements as 1) refractory concrete mix must have good placeability, 2) its dried castings must have homogeneous structure, and 3) to have sufficient strength and minimum shrinkage in service temperature range. Minimally necessary content of bonding suspension (CAP mechano-chemical binder) in concrete mixes as P_2O_5 carrier is preferably. High P_2O_5 concentration in CAP concrete compositions is undesirable because phosphorus anhydride has a destabilizing effect on the strength properties at high temperatures. Tab. 1 lists compositions used in dense refractory concretes.

Tab.1:
Composition of CAP concrete mixes

Concrete mix constituents	Constituents content in concrete mix, %			
	Mix indexes			
	VC-1	VC-2	VC-3	VC-4
	C-1	C-2	C-3	C-4
CAP bonding suspension	20	25	30	40
Fused and sintered corundum aggregate				
2–0,5 mm fraction	60	60	60	60
< 0,5 mm fraction	20	15	10	-

It is necessary to note that VC mixes are the vibro-casted by the consistency, C mixes - casted. At the same time in specimens structure obtained from the VC-3 and C-3 mixes insignificant disintegration occurs whereas C-4 specimens structure exhibits clear disintegration occurring between the aggregate settled grains and fine-disperse suspension. It determines the castings deformation during a drying due to the different shrinkage of these layers. Increasing the suspension content in mixes of 20% to 40% increases the P_2O_5 amount of 0,093 to 0,185% and improves setting properties of CAP concretes at that on conversion of vibro-casted to casted mixes (Fig.1). Further

increasing the suspension content produces lower strengths of concrete castings result from their disintegration.

The above requirements determined emphasizes that C-4 mix containing 40% of bonding suspension and 60% of the fused and sintered corundum aggregate is more optimal for further evaluation of CAP concretes.

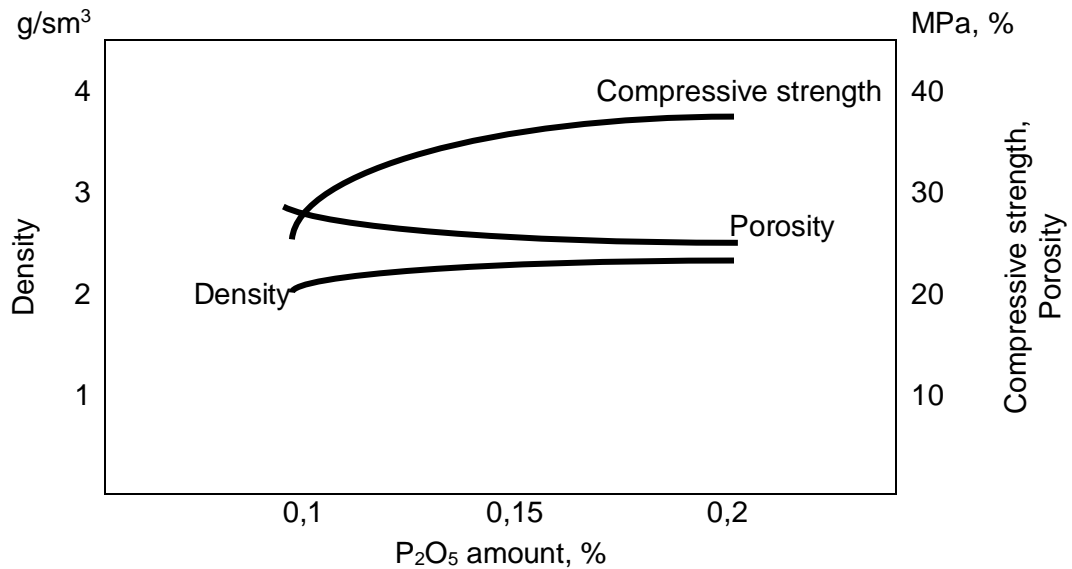


Fig.1: Effect of P₂O₅ amount on properties of CAP concretes

Results and discussion

The previously discussed problem associated with the loss in mechanical strength on setting time preclude the use of HA and CAP hydraulically setting cements. Lower strength of HAC and CAPC hardening coagulative matrices in comparison with the crystalline in the 300^o to 900 °C range deters their use for obtaining fired-strength properties [5]. Unlike hydraulically setting cements, mechano-chemical binder (suspension) contains less than 1% of colloidal component (Fig. 1) and relatively great amounts of hydroxyl groups have no effect on shrinkage and mechanical-strength properties of concretes bonded with CAP suspension, that is, the loss in strength and restructuring on heating do not occur [4].

Evaluation of CAP refractory concretes is directly related to the influence of phosphate-containing phases being formed within bonding suspension on thermal-mechanical properties. The thermal-shock-damage resistance represented by the corundum concrete bonded with CAP mechano-chemical binder is illustrated in Fig. 2. The high cold MOR obtained on specimens fired at 1400 °C can be explained the presence at the intergranular boundaries of the phosphate-containing gel-shaped phases which are transformed into glassy interlayers mostly AlPO₄ (berlinite or cristobaphite). AlPO₄ extension in the 600^o to 800 °C range caused by α→β – berlinite conversion (berlinite effect) does not occur on reheating. Since the berlinite thermal expansion coefficient is 6,9·10⁻⁶ 1/°C at 900 °C, its crystallization at >1100 °C is accompanying with the concretes loosening that provides to develop the microcrack structure enabling to relax thermal stresses on subsequent thermal cycling.

The better thermal-shock-damage resistance of corundum concrete bonded with CAP mechano-chemical binder is ascribed to the <5 – 10-μm closed pores which are

thought to perform as crack arrestors and better mechanical bonding to the rougher concrete fractured surfaces. Besides increasing the strength value of the concrete bonded with CAP suspension would explain the more efficient use of the mechano-chemical bonding compared with hydraulically setting cement wherein some of the CAPC is lost in the large open pores of coarse grains.

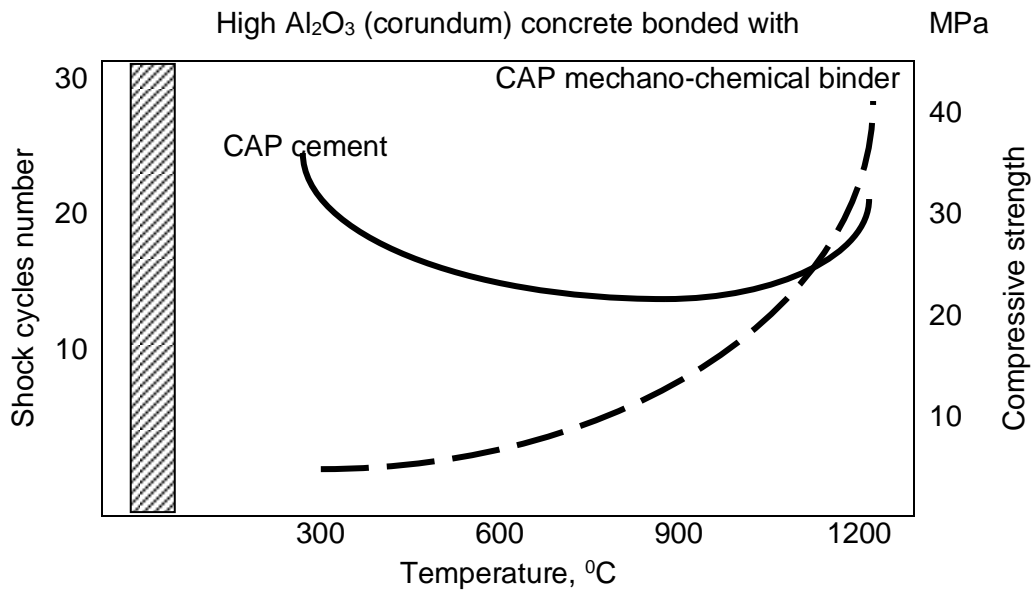


Fig.2: Comparative thermal-shock-damage resistance of CAP concretes

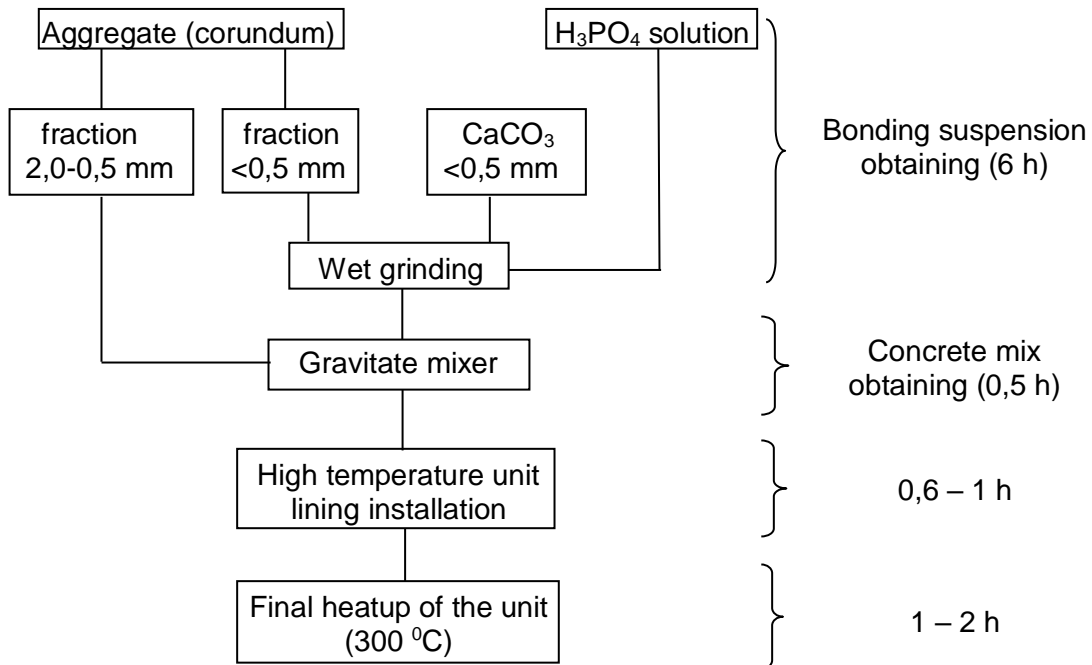


Fig.3: The installation technological scheme of concrete lining bonded with CAP mechano-chemical binder

The use of refractory concrete bonded with CAP mechano-chemical binder provides the significantly quick installation of lining because the initial strength developing requires no setting time in contrast to the concrete bonded with CAP cement. The desired structural integrity and strength development are mostly achieved during the dryout and heatup of the unit as shown in Fig. 3. These processing steps are not accompanying with additional shrinkage and the loss in strength in the 300^o to 900 °C range compared with CAPC concrete.

The CAP refractory concretes obtained retain their volume integrity when subjected to prolonged periods of cyclic heating and cooling (after 30 shock cycles) present in high temperature industrial processes. The CAP refractory concretes can be used for refractory applications 1700 °C. They require only a drying at 300 °C and 2 h to develop sufficient strength of lining while a heatup within 8-10 h contributes to the hot strength >40 MPa.

Conclusions

We conclude that further advances will be possible in meeting the future challenges for new types of refractories in many industries. The meaningful thermal-shock-damage resistance and high fired-strength obtained on the corundum compositions bonded with CAP mechano-chemical binder explain why these systems are performing so well in industry, as illustrated in high Al₂O₃ lining being used to the coals gasifying unit (Fig. 3). Unquestionably, the high concentrated bonding suspensions (HCBS) for refractory concretes will become more available with a subsequent increased interest in their properties.

References

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