

An Effective Cleaning Method of Cement Clinker from Alkaline Earth Metals

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Abstract: “Quattamia cement plant” (Suez Cement Company) uses as raw materials a local Q clay, red clay and limestone. The largest part of alkalies contains Q clay (9.58%). Daily clay input makes up 2292 t and accordingly 95 t d⁻¹ alkalies draws into cement kiln, the biggest part into by-pass dust which contains minerals (galite, thermonatrit) with dimensions 23-52 mcm. The alkalies’ presence leads to cement strength and water proof decreasing. The problem solution consists of using the Multiproductive Staged Classifiers (MSC) which permits to divide any powder into some necessary fractions according to particles’ density and dimension. Experimentally Q clay was being cleaned from alkalies using 3-staged MSC. The first stage catches clay particles, the second sulfates, the third chlorides, oxides and hydroxides. Light particles caught by filter. Using 2-staged MSC for BPD classification permitted to get 89.37 mass % of clinker-forming materials and 9.41 mass % of alkalies, small particles were caught by filter. Carried out investigations and natural testing convince in possibilities: of cleaning Q clay from alkalies that leads to cement quality rising as much as approximately 20% and BPD cleaning from alkalies that results in 90% clinker-generated return to cement production as raw materials, environment protection is fulfilled in both cases.

Key words: Clay, cement, analysis, methods, cleaning

INTRODUCTION

Quattamia cement plant uses as raw materials a local Quattamia clay (Q clay), red clay and limestone. According to plant laboratory data the chemical composition raw materials can be seen in Table 1. It has been counted over again from mass % to mole % and included it to Table 1.

The data show the largest part of alkalies contains Q clay which keeps 9.58% those components. Red clay contains 4% alkalies and limestone only 0.54%. Besides that daily clay input makes up 2292 t and accordingly 95 t d⁻¹ alkali components draws into cement kiln. A small part of alkalies gets into cement clinker, the big part into By-Pass Dust (BPD) and the last pulverize in the air.

Table 1: Chemical composition Quattamia cement plant raw materials and By-pass dust (Quattamia Cement Laboratory data)

Substances	Quattamia clay (%)		Red clay (%)		Limestone (%)		By-pass dust (%)	
	Mass	Mole	Mass	Mole	Mass	Mole	Mass	Mole
K ₂ O	1.300	0.033	1.500	0.0160	0.080	0.010	5.00	0.053
Na ₂ O	2.840	0.046	1.800	0.0290	0.130	0.010	1.79	0.029
Cl	0.570	0.016	0.360	0.0100	0.080	0.020	6.80	0.192
SO ₃	4.870	0.061	0.340	0.0040	0.250	0.030	8.14	0.102
Alkalies	9.580	0.560	4.000	0.0464	0.250	0.025	21.73	0.294
SiO ₂	46.200	0.770	55.480	0.9250	2.610	0.044	14.63	0.244
Al ₂ O ₃	12.100	0.119	19.520	0.1910	0.900	0.009	4.42	0.043
Fe ₂ O ₃	5.560	0.034	9.680	0.0610	0.500	0.003	1.96	0.012
CaO	11.500	0.205	0.940	0.0170	52.500	0.938	53.81	0.961
MgO	1.950	0.048	0.580	0.0140	0.970	0.024	0.68	0.017
Clinker-generated	77.310	1.176	86.200	1.2080	57.480	1.018	75.50	1.277
Alkalies before evaporation								
NaCl	0.936	0.016	0.585	0.0100	0.117	0.002	3.39	0.029
KCl	-	-	-	-	-	-	7.90	1.060
KOH	1.460	0.020	-	-	-	-	-	-
Na ₂ SO ₄	5.400	0.038	-	-	-	-	-	-
K ₂ SO ₄	4.000	0.023	-	-	-	-	-	-
Others	-	-	-	-	-	-	1.99	0.014

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MATERIALS AND METHODS

The emission spectral analysis peculiarity consists of samples evaporation which leads to its complete destruction. Therefore, one can see such unusual single atoms as Cl and compounds as SO_3 and so on. It has been considered that before thermal destruction alkalies were existed in the form such as salts as NaCl, KCl, Na_2SO_4 , K_2SO_4 and so on. According to above-mentioned salts it is introduced in Table 1 a section "Alkalies before evaporation". One can see how much alkalies contain both Q clay and BPD.

It was necessary to know what form have alkalies amidst clay are they connected with other particles or not. Microscopy can diagnose problems in clinker production and can point to solution in the case of coarse particles in the raw feed (Klassen *et al.*, 2013; Luginina *et al.*, 2013a, b; Karikov *et al.*, 2013; Klassen, 2013; Borisov *et al.*, 2012), especially electronic microscopy. Examination of electronic pictures has shown that mineral crystals galite, thermonatrite and so on can be seen amidst Q clay particles. A sample was heat treated at the 300°C and milled. The electronic still pictures of clay powder show that there are lonely mineral crystals with rectangular facets amidst clay particles. Their dimensions are from 23-52 μm , they are not connected with clay particles. It is obvious they enter Q clay from dry salt rains characteristics to Egypt.

Those pictures are convinced of probability alkalies extraction from Q clay in proper conditions. Let us consider what damage to cement is accompanied by alkalies presence in the raw materials. Alkalies are lightly melting substances. Their presence leads to early melt formation (800°C) simultaneously with CaCO_3 decarbonization beginning at 825°C . In consequence alkalies melt migration to new formatted porous CaO media originated by decarbonization process there exists a reaction between SiO_2 , Na^+ , K^+ which leads to Na_2SiO_3 , K_2SiO_3 formation which are very viscous and can penetrate into porous CaO at temperature $>1089^\circ\text{C}$. Thus some pores will be shut off which prevents $\text{CaO}+\text{SiO}_2$ reactions proceeded at $1400-1450^\circ\text{C}$. Those processes lead to appearance some defects in the clinker amount of which is proportional to the alkalies content in raw materials. As a result of alkali compounds presence in raw materials the cement strength and water proof are decreasing. These reasonings show the necessity of Q clay cleaning from alkali components (Borisov and Mandrikova, 2012; Mandrikova and Borisov, 2013a, b).

There are few methods to clean any clays from alkalies. The first using high water alkalies solubility. We even shall not discuss these methods because of their

complexity and expensiveness. The second using density differences of clay components. In this case, we have to be certain that alkali components are not associated with clay particles. We can be convinced of that only by examination electronic photo where each galite crystal is seen apart from clay crystals.

An approach to that problem solution consists of using a new created Multiproductive Staged Classifiers (MSC) and classifying technology (Klyuchnikova, 2012) which permits to divide any powder on some necessary fractions according to particles density and dimension.

The MSC separation process carried out in the rising air-powders stream thanks to staged stream velocity diminishing which is achieved by consistent classifier channel diameters increasing. The inner stage diameters are calculated according to experimental data. The scheme of four-staged MSC is shown on Fig. 1. The principle of MSC function consists in balance between gravity G and lifting L forces. There are three cases for forces correlation:

- $G < L$: a particle is lifting
- $G = L$: a particle is soaring
- $G > L$: a particle is sinking down

The dependence of lifting forces from air velocity V has a shape presented on Fig. 2 where, $V_0 > V_1 > V_2 > V_3 > V_4$ air velocities in the stages.

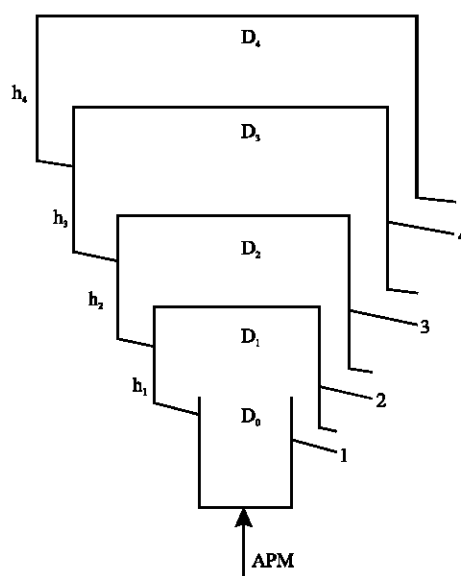


Fig. 1: Four-staged MSC scheme; D_0 : entrance pipe diameter; D_1, D_2, D_3, D_4 : stage diameters; h_1, h_2, h_3, h_4 : stage height; 1, 2, 3, 4: unload tubes; APM: air-powder mixture

Let us imagine that in air stream presents some four particle kinds of different weight G : $G_1 > G_2 > G_3 > G_4$ and all of them less than lifting force L_0 . These particles will rise with different velocities. Light particles have larger rising velocity. Then we decrease the air velocity in such a way that particles G_1 starts moving down when particles G_2, G_3, G_4 continue moving upwards. We catch particles G_1 in a trap. The new composition of air powder moves upwards and we decrease air velocity once more. Particles G_2 change moving direction: they begin sinking down and a trap for G_2 is prepared. And so on for G_3 and G_4 .

But, in reality a powder consists of many particles of different size and density. Therefore, it is better to divide particles on some fractions. For that purpose we diminish the air stream velocity stage by stage which permits to get particles fractions distinguished from each other by particle sizes and densities. For diminishing air stream velocity in MSC, we use step by step increasing inner diameter of the tubes which permits to pass from the first type correlation $G > L$ to the second ($G = L$) and to third ($G < L$) which leads to sequentially, particles sedimentation with decreasing gravity forces.

The ideal powders for classification are monomineral or monodispersed. In the first case all particles have the same densities but their dimensions differ; in the second case, particles have the same dimensions but differ by densities. Monomineral and monodispersed powders can be easily separated on any necessary fractions. But, often particles have both distinctions: by densities and

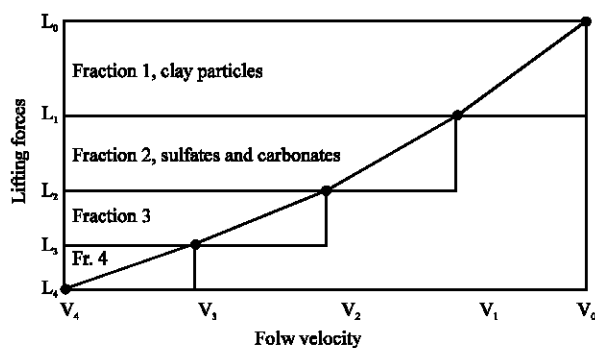


Fig. 2: Dependence of lifting forces L on flow velocity V

dimensions. Such distinctions have Q clay and BPD. For those cases it is necessary to calculate the dependencies between Classifying Index (CI) and particle dimensions. For those purposes, one can use an equation $CI = (pd)^{0.5}$ which permits to determine stages amount and borders between fractions (p : density, d : diameter of particles).

RESULTS AND DISCUSSION

Main part: The dependence CI from particle sizes for the main Q clay substances is shown on Fig. 3. According to Fig. 3, undestroyed clay particles have $CI > 0.407$, sulfates and carbonates have CI from 0.285-0.4, NaCl, KCl, NaOH, CaOH, Na_2O , K_2O have CI from 0.223-0.33. Such CI distribution shows possibility to use 3-staged MSC. The first stage catches clay particles, the second sulfates and carbonates and the third chlorides, sodium and potassium oxides and hydroxides. Light particles with $CI < 0.22$ have caught by filter.

The Q clay cleaning from alkalis is decisive not for only ecological problems but at the same time it leads to cement hardness rising. We tested some laboratory samples made from natural Q clay and Q clay cleaned from alkalis. The other components were red clay and Belgorod chalk with correlation 28% Q clay, 5% red clay, 67% chalk (Table 2). Always we could see the cement samples hardness made of cleaned Q clay was no $< 20\%$ bigger than those samples made of natural Q clay.

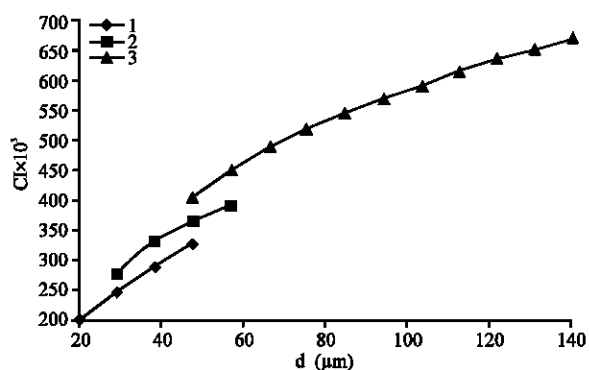


Fig. 3: Dependence of classifying index CI on particle size.
1: alkalies; 2: sulfates and carbonates; 3: clay particles

Table 2: Quattamia clay cleaning influence on the cement hardness

The raw material composition				The hardness ($kg\ sm^{-2}$)					
Quattamia clay				Crook (days)			Compress (days)		
Natural	Cleaned from alkalis	Red clay	Chalk	3	7	28	3	7	28
28	-	5	67	22.1	24.3	59.2	58	178	401
-	28	5	67	31.3	38.7	62.3	181	260	512

Table 3: Q clay classifying factors and results

Stages	The substances	Particle dimensions (μm)	Density (kg m^{-3})	CI $\times 10^3$	Product output (%)
1	Clay	>70	3200	>470	89.1
2	Na_2SO_4 , K_2SO_4 , Na_2CO_3 , K_2CO_3	30-60	2700	285-400	9.4
3	NaCl , KCl , NaOH , KOH , Na_2O , K_2O	23-52	2150	223-330	1.3
		-	2044	-	-
Filter	Light admixtures	<23	2044	<220	<0.2

Table 4: BPD substances properties

Substances	Density (kg m^{-3})	Particle dimensions (μm)	CI $\times 10^3$	The utilization direction
Fe_2O_3	5240	30-70	397-606	Clinker forming materials
SiO_2	2650	30-120	342-684	
CaO	3370	40-70	367-486	
CaSO_4	2990	50-100	387-547	
MgO	3580	40-70	378-501	
Al_2O_3	3900	30-90	397-593	Alkali solution receptions
NaCl	2165	20-50	208-329	
KCl	1999	20-50	200-316	
$\text{Ca}(\text{ClO}_2)_2$	2700	20-40	232-328	

Table 5: BPD classification results

The substances	Densities (kg m^{-3})	Particle dimensions (μm)	CI $\times 10^3$	Stage	Products output (%)
Clinker-forming materials	2320-5240	30-120	342-684	1	89.37
Alkalies	1999-2700	20-50	200-329	2	9.41
Small particles	-	<20	<200	Filter	1.22

The cleaning Q clay from alkali components require three-four MSC with 50th^{-1} productivity. We classified Q clay sample by 3-staged MSC and got four fractions. The last fraction was caught by filter (Table 3). The first three fractions differed from each other by densities and had very small water soluble components. The filter caught all light components that contained alkalies.

Resume: In virtue of carried out investigations and natural testing the following possibilities have been determined:

- Cleaning Q clay from alkalies which leads to cement quality rising as much as $\sim 20\%$
- BPD cleaning from alkalies which results in 90% clinker generated return to cement production as raw materials, environment protection fulfilled by both cases

CONCLUSION

According to Quattamia plant data clinker generated substances make up 75.5% of BPD. It is correct to add to clinker generated substances CaSO_4 which put together about 90% clinker generated. Table 4 contains BPD substances including CI.

As one can see clinker generated and alkalies differ from each other by CI. For clinker generated the CI values change from 0.342-0.684, for alkalies from 0.2-0.329. That difference permitted to divide very easily clinker generated and alkalies by means of experimental 3-staged MSC where the second stage was shut up. The results of BPD classifying is presented in Table 5.

According to Table 5, 2-staged MSC permits to classify BPD in two fractions and get 89.37 mass% clinker-forming materials and 9.41 mass% alkalies. Water solubility was also tested. Clinker generated fraction water solubility was 0.307%, alkalies 34.8%.

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