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Development of the composition of CAC 35 alumina cement clinker based on local raw materials

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Разработка состава глинозёмного цементного клинкера CAC 35 на основе местного сырья

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Abstract

This article examines the formation of the raw material mixture composition for producing CAC 35 alumina cement clinker based on local mineral raw materials. The mineralogical composition of calcium aluminate cements and the conditions for forming the main clinker phases — calcium monoaluminate (CA), calcium dialuminate (CA_2), and $C_{12}A_7$, which determine the properties of alumina cement, are analyzed. The possibility of using Al_2O_3-rich mineral raw materials, limestone, and corrective components is substantiated. When selecting the raw material mixture composition, the influence of the CaO-to-Al_2O_3 ratio, as well as the contents of SiO_2 and Fe_2O_3, on the mineralogical composition of the clinker is considered. X-ray fluorescence and X-ray diffraction analyses are proposed to determine the chemical and mineralogical composition of the clinker. The research results may contribute to assessing the technological feasibility of producing CAC 35 clinker from local raw materials, rational resource utilization, improved production efficiency, and reduced cement production costs. Particular attention is given to achieving the required phase composition and technological characteristics of the final material. Optimizing component ratios enables controlled formation of aluminate phases, improved cement performance, and stable quality during industrial production and application.

Аннотация

В данной статье рассмотрены вопросы формирования состава сырьевой смеси для получения глиноземистого цементного клинкера ГЦ 35 на основе местного минерального сырья. Проанализированы минералогический состав кальциевых алюминатных цементов и условия образования основных клинкерных фаз — моноалюмината кальция (CA), диалюмината кальция (CA_2) и $C_{12}A_7$, определяющих свойства глиноземистого цемента. Обоснована возможность использования богатого Al_2O_3 минерального сырья, известняка и корректирующих компонентов. При выборе состава сырьевой смеси рассмотрено влияние соотношения CaO и Al_2O_3, а также содержания SiO_2 и Fe_2O_3 на формирование минерального состава клинкера. Для определения химического и минералогического состава предусмотрено применение рентгенофлуоресцентного и рентгенодифракционного анализа. Результаты исследования могут способствовать оценке технологической возможности получения клинкера ГЦ 35 на основе местного сырья, рациональному использованию ресурсов, повышению эффективности производства и снижению себестоимости цемента. Особое внимание уделено обеспечению требуемого фазового состава и основных технологических характеристик получаемого готового материала. Установление оптимального соотношения компонентов позволяет целенаправленно регулировать образование алюминатных фаз, улучшать эксплуатационные свойства цемента и обеспечивать стабильность его качества при промышленном производстве и эксплуатации.

Keywords: alumina cement, calcium aluminate cement, CAC 35, cement clinker.

Ключевые слова: глиноземистый цемент, кальциевый алюминатный цемент, ГЦ 35, цементный клинкер.

Introduction

Calcium aluminate cements (CAC) differ significantly from Portland cements in terms of their mineralogical composition. In their clinker, the main binding phases include monocalcium aluminate (CA), calcium dialuminate (CA_2), and, in some cases, phases such as $C_{12}A_7$ [1, 2]. Scientific sources identify the CA phase as an important mineral component of calcium aluminate cements [5].

The book *Lea's Chemistry of Cement and Concrete*, edited by Hewlett and Liska, provides a detailed discussion of the chemical composition, production technology, hydration, and applications of calcium aluminate cements [1]. In this source, the abbreviated chemical formula of CA is given as $CaO \cdot Al_2O_3$, and calcium aluminate cements are classified as a group of special cements [1].

Although calcium aluminate cements were initially developed as sulfate-resistant cements, they are currently also used for rapid setting, high-temperature resistance, resistance to abrasive wear, and in special repair materials [5, 6].

From this perspective, the development of the composition of CAC 35 alumina cement clinker based on local raw materials is important not only technologically but also economically.

Research Objective

The main objective of the study is to develop an appropriate raw material composition for CAC 35 alumina cement clinker using local Al_2O_3-rich mineral raw materials, limestone, and corrective components.

To achieve this objective, the following tasks were established: determination of the chemical composition of local raw material samples; selection of Al_2O_3-rich components; determination of the optimal ratio of CaO and Al_2O_3; investigation of the formation conditions of CA, CA_2, and $C_{12}A_7$ phases in the clinker; determination of the firing regime of the raw material mixture; evaluation of the mineralogical and physical-mechanical properties of the resulting clinker.

Materials and Methods

The chemical analysis of the clinker was carried out using a Rigaku NEX CG energy-dispersive X-ray fluorescence spectrometer (USA).

X-ray diffraction analysis was performed based on diffraction patterns obtained using an XRD-6100 (Shimadzu, Japan) instrument.

The strength and setting time of the cement stone were determined in accordance with GOST 30744-2001. The chemical composition of the raw materials is presented in Table 1 [1].

Mineralogical Composition of Alumina Cement Clinker

The main mineral components of calcium aluminate cements are CA, CA_2, and $C_{12}A_7$ [1, 2, 5]. Their amounts depend on the ratio of CaO to Al_2O_3 in the raw material composition, as well as on the amounts of additional oxides such as SiO_2 and Fe_2O_3.

The formation reaction of monocalcium aluminate can be expressed in simplified form as follows:

$$CaO + Al_2O_3 \rightarrow CaAl_3O_4$$

or, in the abbreviated notation used in cement science:

$$C + a \rightarrow CA$$

This phase is considered one of the important hydraulically active components in calcium aluminate cements [1, 5].

CA_2 is formed according to the following reaction:

$$CaO + 2Al_2O_3 \rightarrow CaAl_4O_7$$

The $C_{12}A_7$ phase is one of the important components of the high-alumina calcium aluminate system, and its presence can significantly affect the setting process of cement [2, 5].

Scientific studies have shown that the hydration process of calcium aluminate cements is complex and that hydration products vary depending on temperature and moisture conditions [7]. In particular, the transformation of metastable hydrates into stable phases may affect the later-age strength of the cement stone [7,].

Selection of Local Raw Materials

When selecting raw materials for CAC 35 clinker, the main criteria are their chemical composition and their ability to provide the required oxides. Al_2O_3 is the most important component for alumina cement [1, 2].

Bauxite, alumina-rich clay, and other aluminum-containing mineral rocks can be used as sources of Al_2O_3.

Limestone serves as the main source of CaO. During the firing process:

$$CoCO_3 \rightarrow CaO + CO_2$$

As a result of this reaction, free CaO is formed, which reacts with Al_2O_3 to form calcium aluminate phases.

It is important to control the amount of SiO_2 in the raw material composition. In calcium aluminate cements, silicon oxide is generally present in limited amounts, because an increase in its content may lead to the formation of aluminosilicate phases such as C_2AS [1, 5].

Results and discussion

Calculation of the Raw Material Mixture.

Table 1. Chemical composition of the main raw materials

Raw material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Other oxides	SO_3	L.O.I.
Limestone	3.0	1.5	1.0	50.0	1.2	1.1	0.2	42.0
Kaolin (AKF 78)	55.0	30.0	0.8	0.2	0.5	1.3	0.2	12.0
Granule (Shurtangaz)	0.2	89.0	0.1	0.4	0.2	2.0	0.1	8.0
Iron-containing industrial waste of Almalyk Mining and Metallurgical Complex	25.0	7.0	44.0	3.0	1.5	17.3		

Analyzed result(FP method, Scatter)

No.	Component	Result	Unit	Stat. Err.	LLD	LLQ
1	Cl	0.0854	mass%	0.0004	<0.0001	0.0003
2	Al2O3	34.7	mass%	0.0312	0.0047	0.0141
3	SiO2	56.9	mass%	0.0321	0.0830	0.249
4	SO3	0.109	mass%	0.0012	0.0019	0.0057
5	K2O	1.34	mass%	0.0094	0.0062	0.0186
6	CaO	0.231	mass%	0.0036	0.0054	0.0161
7	TiO2	0.506	mass%	0.0032	0.0017	0.0050
8	V2O5	0.0252	mass%	0.0011	0.0027	0.0082
9	MnO	0.0113	mass%	0.0007	0.0017	0.0051
10	Fe2O3	0.738	mass%	0.0017	0.0006	0.0019
11	CuO	0.0040	mass%	0.0001	0.0002	0.0005
12	ZnO	0.0319	mass%	0.0003	0.0001	0.0003
13	Ga2O3	0.0071	mass%	0.0001	0.0002	0.0006
14	As2O3	0.0013	mass%	0.0001	0.0004	0.0012
15	SeO2	0.0004	mass%	<0.0001	<0.0001	0.0002
16	Rb2O	0.0101	mass%	<0.0001	<0.0001	0.0002
17	SrO	0.0042	mass%	<0.0001	<0.0001	0.0002
18	Y2O3	0.0105	mass%	<0.0001	0.0001	0.0004
19	ZrO2	0.142	mass%	0.0008	0.0004	0.0013
20	Nb2O5	0.0066	mass%	0.0003	0.0004	0.0011
21	SnO2	0.0015	mass%	0.0001	0.0003	0.0009
22	BaO	0.0049	mass%	0.0005	0.0013	0.0038
23	WO3	0.0062	mass%	0.0003	0.0008	0.0023
24	Ir2O3	(0.0018)	mass%	0.0002	0.0007	0.0020
25	PtO2	0.0010	mass%	0.0001	0.0003	0.0009
26	Au2O	0.0008	mass%	<0.0001	0.0002	0.0007
27	PbO	0.0210	mass%	0.0002	0.0002	0.0005
28	La2O3	0.0152	mass%	0.0009	0.0021	0.0064
29	CeO2	0.0151	mass%	0.0011	0.0027	0.0081
30	Eu2O3	0.0581	mass%	0.0016	0.0029	0.0086
31	Dy2O3	(0.0089)	mass%	0.0013	0.0037	0.0110
32	U3O8	0.0014	mass%	<0.0001	0.0003	0.0008

Figure 1. Chemical composition of Angren kaolin (AKF 78) obtained using a Rigaku spectrometer

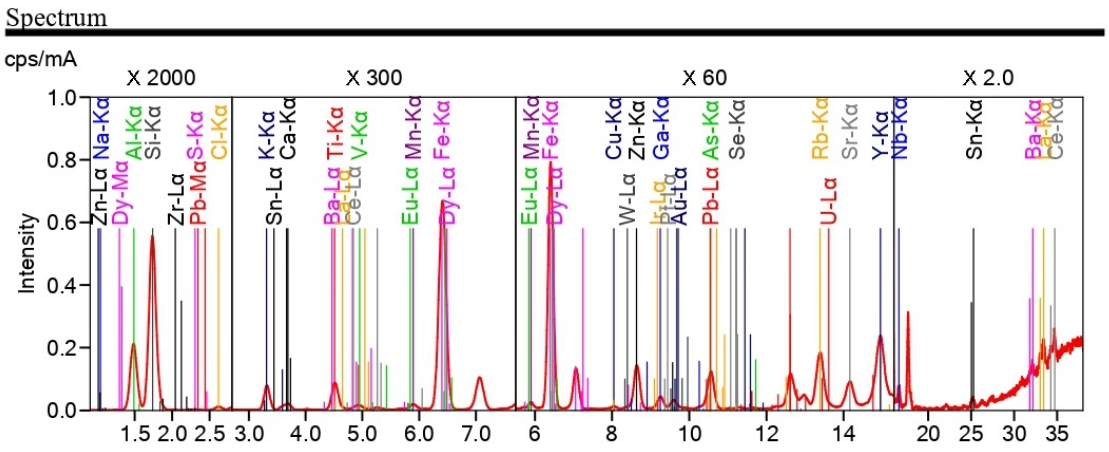


Figure 2. Chemical composition of Angren kaolin (AKF 78) obtained using a Rigaku spectrometer

When calculating the raw material composition of CAC 35 clinker, primary attention is paid to the ratio between CaO and Al_2O_3. The final composition of the raw material should be determined based on the chemical analysis of actual samples from the relevant deposits or quarries.

For laboratory experiments, several mixture variants consisting of Al_2O_3-rich raw materials, limestone, and corrective components can be prepared.

Table 2. Composition of the raw material mixture

Oxide	**Mass content, %**
SiO_2	14.7
Al_2O_3	27.6
Fe_2O_3	5.5
CaO	24.0
MgO	0.9
Other oxides	4.5
SO_3	0.15
L.O.I.	23.9

Table 3. Composition of the raw material mixtures

Raw material	**Mixture 1, %**	**Mixture 2, %**	**Mixture 3, %**
Limestone	47	47	45
Kaolin (AKF 78)	22	19	16
Granule (Shurtangaz)	23	23	23
Slag	8	11	16
Total	**100**	**100**	**100**

Table 4. Main chemical and mineralogical composition of the clinker

Chemical composition	**Content, %**	**Mineralogical composition**	**Content, %**	**Name**
CaO	33.6	CA ($CaAl_2O_4$)	50–60	Monocalcium aluminate
Al_2O_3	36.9	CA_2 ($CaAl_4O_7$)	10–20	Monocalcium dialuminate
SiO_2	21.0	$C_{12}A_7$ ($12CaO·7Al_2O_3$)	5–15	Calcium aluminate
Fe_2O_3	6.1	C_2S ($2CaO·SiO_2$)	5–10	Belite
—	—	C_2AS	5–10	Gehlenite

Analyzed result(FP method, Scatter)

No.	Component	Result	Unit	Stat. Err.	LLD	LLQ
1	Cl	0.0342	mass%	0.0003	0.0002	0.0006
2	Ac	0.0028	mass%	0.0002	0.0006	0.0019
3	MgO	0.666	mass%	0.0196	0.0434	0.130
4	Al2O3	36.9	mass%	0.0350	0.0185	0.0556
5	SiO2	21.0	mass%	0.0236	0.0087	0.0260
6	SO3	0.197	mass%	0.0016	0.0024	0.0072
7	K2O	0.399	mass%	0.0053	0.0074	0.0223
8	CaO	33.6	mass%	0.0381	0.0244	0.0731
9	TiO2	0.245	mass%	0.0034	0.0048	0.0143
10	V2O5	0.208	mass%	0.0025	0.0036	0.0107
11	Cr2O3	0.0063	mass%	0.0007	0.0019	0.0056
12	MnO	0.0751	mass%	0.0016	0.0024	0.0073
13	Fe2O3	6.11	mass%	0.0056	0.0098	0.0294
14	CuO	0.0688	mass%	0.0008	0.0007	0.0022
15	ZnO	0.192	mass%	0.0011	0.0009	0.0027
16	Ga2O3	0.0040	mass%	0.0002	0.0004	0.0012
17	As2O3	0.0032	mass%	0.0002	0.0007	0.0020
18	Rb2O	0.0024	mass%	<0.0001	<0.0001	0.0003
19	SrO	0.0157	mass%	0.0001	0.0002	0.0006
20	Y2O3	0.0052	mass%	<0.0001	0.0001	0.0003
21	ZrO2	0.177	mass%	0.0026	0.0026	0.0077
22	MoO3	0.0272	mass%	0.0026	0.0034	0.0103
23	Sb2O3	0.0045	mass%	0.0004	0.0007	0.0022
24	BaO	0.0153	mass%	0.0011	0.0025	0.0074
25	Ir2O3	(0.0012)	mass%	0.0004	0.0010	0.0031
26	PbO	0.0257	mass%	0.0004	0.0005	0.0016
27	Dy2O3	(0.0165)	mass%	0.0050	0.0151	0.0452

Figure 3. Chemical composition of CAC 35 clinker obtained using a Rigaku spectrometer

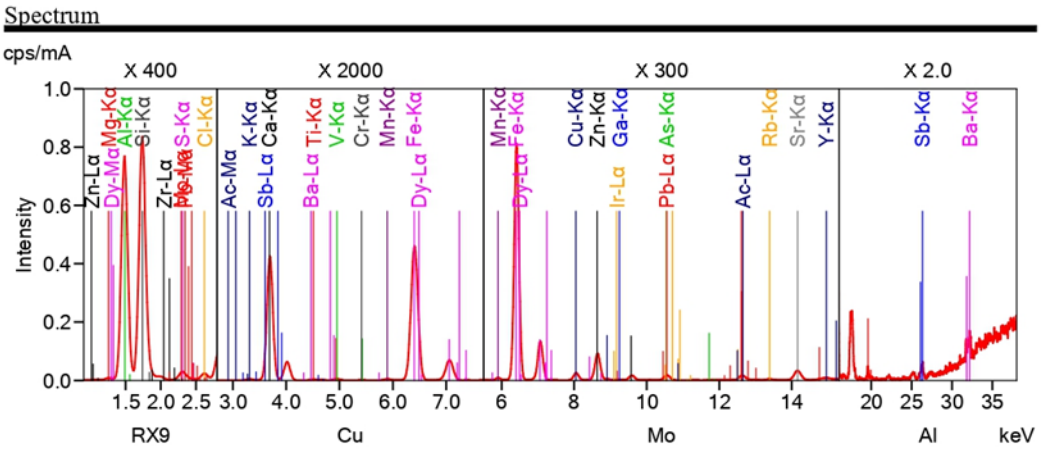


Figure 4. Chemical composition of CAC 35 clinker obtained using a Rigaku spectrometer

Clinker Formation Process. After being crushed and homogenized, the raw material mixture is sent to the firing process. Initially, moisture evaporation, decomposition of clay minerals, and decarbonization of limestone occur. At the subsequent stage, solid-state reactions between CaO and Al_2O_3 intensify.

Therefore, for CAC 35 clinker, it is advisable to determine the optimal firing regime by conducting experiments at several temperature points.

Clinker Quality Assessment. X-ray diffraction analysis is recommended for determining the mineralogical composition of the resulting clinker. This method makes it possible to identify the presence of CA, CA_2, $C_{12}A_7$, and other phases [1, 5].

X-ray fluorescence analysis or conventional chemical methods can be used to determine the chemical composition [9].

For the prepared cement samples, the following parameters should be determined: standard consistency; initial and final setting time; water demand; volume stability; compressive strength; early-age and later-age strength; resistance to thermal effects.

The rapid development of strength in calcium aluminate cements is reported as one of their important advantages [5, 6]. However, scientific studies have shown that phase transformations of hydrates and the “conversion” process may affect long-term strength [7.8].

In the development of CAC 35 alumina cement clinker, one of the main tasks is to maintain a high Al_2O_3 content in the raw material composition while ensuring an optimal amount of CaO.

A deficiency of CaO may limit the formation of CA and lead to an increase in the proportion of CA_2. An excessive amount of CaO, in turn, may increase the possibility of free CaO remaining in the clinker or the formation of other calcium-rich phases.

Conclusion

The development of CAC 35 alumina cement clinker based on local mineral raw materials is a technologically and economically promising direction.

In developing the clinker composition, Al_2O_3-rich raw materials and limestone should be selected as the main components, while the amounts of SiO_2 and Fe_2O_3 should be controlled to ensure the target mineralogical composition.

According to the research results, the main active phases of the clinker may consist of CA, CA_2, and $C_{12}A_7$. Their proportions depend on the raw material composition and firing regime [1, 5].

The use of local raw materials makes it possible to reduce the need for imported components, optimize transportation costs, and ensure the efficient use of regional mineral resources.

In further studies, it is recommended to determine the exact chemical composition of local bauxite, clay, and limestone, calculate several raw material formulations, produce clinker at different firing temperatures, and determine the optimal CAC 35 composition using XRD and physical-mechanical tests.

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