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Hydration of alinite cement produced from soda waste sludge

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HIGHLIGHTS

- Hydration of alinite cement produced from soda waste yielded cementitious products.
- Hydration of alinite cement did not practically stop during induction (dormant) period.
- Increasing gypsum content in the cement up to 12% increased compressive strength.
- Formation of C-S-H gel and Friedel's salt-like phase was observed in SEM images.
- Presence of portlandite appeared to be dependent on clinker's phase composition.

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ABSTRACT

Alinite cement is an alternative inorganic, low-energy binding material. This experimental study investigated hydration characteristics of alinite cement which was produced by using soda waste sludge as a raw material. Paste microstructures were studied by X-ray powder diffraction and scanning electron microscopy. Heat of hydration and compressive strength values were also determined. Formation of C-S-H gel and calcium chloroaluminate hydrates which resemble Friedel's salt was observed. Induction period of alinite cement was around 15–20 min and unlike Portland cement, hydration did not practically stop during this period. Up to 12% gypsum addition to alinite cement resulted in increased compressive strength.

1. Introduction

Increasing environmental awareness had made the search for utilizing industrial wastes an important concern for both the manufacturers and the researchers. One promising approach is to produce low-energy cements by using industrial wastes as raw and/or partial Portland cement replacement materials. Use of materials like fly ash, ground granulated blast furnace slag, natural pozzolans, limestone powder, etc. as partial cement replacement materials is one of the common alternatives that are being used, currently. Still, possibilities of producing other low-energy alternative cements are being studied. Calcium sulfoaluminate-belite cements and magnesium oxide-based cements are considered as possible alternatives although their use is comparatively much smaller than those of Portland cement based cements. Besides these, alinite cement was developed in former USSR in the 1970s and patented in 1977 [1].

Alinite cement clinker is obtained from a raw material mixture that contains limestone, clay, magnesium oxide (MgO) and calcium chloride ($CaCl_2$). The raw mixture is calcined at 1000–1300 °C [2,3]. The resulting clinker has a more porous structure and is softer than the Portland cement clinker. Production of alinite cement results in approximately 30% less energy consumption than that of ordinary Portland cement (OPC) production [4,2]. The phases in alinite cement clinker are listed in Table 1.

The basic phase is a calcium magnesium oxy-chloroaluminosilicate which is known as alinite. Different chemical formulas were proposed by various researchers for the composition of alinite [5–7]. In a very simple form, it can be written as Eq. (1) [6]. However, it can be more accurately expressed by Eq. (2) [7].

$$Ca_{11}(Si,Al)_4O_{18}Cl \quad (1)$$

$$Ca_{10}Mg_{(1-\frac{x}{2})}\Box_{\frac{x}{2}}\left[(SiO_4)_{\frac{3}{x}}(AlO_4)_{1-x}O_2Cl\right] \quad (2)$$

where 0.35 < x < 0.45 and □ refers to a lattice vacancy.

Alinite is related to alite, which is the main constituent of Portland cements. While alite consists of Ca^{2+}, SiO_4^{4-}, and O^{2-} ions, alinite contains AlO_4^{5-} and Cl^- ions, as well [8]. Generally, CaO content of alinite cement is less than that of Portland cements whereas Al_2O_3 and Fe_2O_3 contents are higher. Hydration of alinite was

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Table 1
Major phases of alinite cement clinker [5].

Phase	Amount (%)
Alinite $\{Ca_{10}Mg_{0.8}[(SiO_4)_{3.4}(AlO_4)_{0.6}O_2Cl]\}$	50–80
Belite (Ca_2SiO_4)	10–40
Calcium chloroaluminate ($Ca_{12}Al_{14}O_{32}Cl_2$)	5–10
Calcium aluminoferrite ($Ca_2(Al,Fe)_2O_5$)	2–10

Table 2
Chemical compositions of the raw materials.

Composition (%, by mass)	DSWS	Clay	Limestone	Iron Ore
Loss on ignition (LoI)	24.85	9.89	42.73	11.70
SiO_2	8.23	56.91	1.97	23.09
Al_2O_3	1.82	14.65	0.68	3.92
Fe_2O_3	1.11	6.22	0.23	55.42
CaO	30.74	5.19	53.24	1.25
MgO	0.49	2.45	1.07	1.07
SO_3	2.48	0.01	<0.01	0.24
Na_2O	3.80	0.84	0.09	0.20
K_2O	0.36	1.94	0.05	0.18
Cl^-	24.92	0.01	0.01	0.02

reported to result in a Friedel's salt-like phase $[Ca_3Al_3O_6{\cdot}CaY_2{\cdot}10H_2O$, where Y is stated as $0.5CO_3^{2-}$, $(OH)^-$, $Cl^-]$ besides C-S-H gel and $Ca(OH)_2$, which are the hydration products of alite, also [7–11]. Furthermore, gypsum addition to alinite cement in order to enhance the strength leads to the formation of ettringite as another hydration product [2,8,12].

Calorimetric studies revealed that early hydration rate of alinite cement is much higher than that of Portland cement and the dormant period that exists in Portland cement hydration is not truly observed in alinite cements [12,7].

Utilization of industrial wastes such as steel plant wastes and municipal incinerator ash as raw meal ingredients for alinite cement production had been investigated [2,11,13–15]. The waste sludge from soda industry also has potential to be used in alinite cement production. Soda ash is an essential material used in glass, detergent, textile, and paper industries. It is produced by a process known as Solvay process. The process results in a waste sludge that contains basically, $CaCO_3$, water, and chlorine. Besides these, $Mg(OH)_2$, SiO_2, Al_2O_3, $CaSO_4$, $Ca(OH)_2$ may be present in small amounts. About 300 kg of sludge is obtained for 1 ton of soda ash production [16].

Previously, Kesim et al. [8] were successful at producing alinite cement by using the filtered form of the waste as the replacement of limestone. As part of the research that also covers the scope of this paper, Uçal et al. [17] were able to produce alinite cement from unfiltered form of the waste, though only partial replacement of limestone was possible due to high chlorine and low calcium content of the waste in its original form. The aim of this experimental investigation is to determine the hydration characteristics of alinite cement produced by using soda waste sludge in its unfiltered form as a raw material.

2. Experimental study

2.1. Raw materials

The raw materials used for the production of alinite cement were dried soda waste sludge (DSWS), clay, limestone and iron ore. Table 2 presents the chemical compositions of the raw materials. The waste was dried to remove the free water prior to the preparation of the raw mixture.

In determining the raw mixture proportions, a previously calculated Portland cement clinker raw mixture of proven performance was used and different replacement levels were tested. It was observed that DSWS failed to completely replace limestone in the raw mixture whereas 30% replacement of limestone with DSWS yielded an alinite cement with mortar compressive strength results comparable to that of Portland cement mortar [17]. However, alinite cement is not likely to be used in applications where high performance is required due to chloride-related concerns, and the primary focus of this research is waste utilization. Therefore, the raw mixture proportions were selected as 39.05% DSWS, 39.05% limestone, 20.61% clay, and 1.3% iron ore, where DSWS replaced 50% (by mass) of the limestone in the mixture.

Table 3
Chemical composition of the alinite cement clinkers (labeled as "A.calcination temperature in °C.calcination duration in hours") [17].

Composition (%, by mass)	A.1050.1	A.1150.1	A.1150.2	A.1150.4
LoI	5.51	1.53	3.63	2.25
SiO_2	18.00	20.23	19.87	20.55
Al_2O_3	5.00	5.07	4.99	5.17
Fe_2O_3	2.45	3.06	3.08	3.30
CaO	40.55	53.40	54.29	55.14
MgO	2.40	2.25	2.20	2.27
SO_3	2.41	1.57	1.65	1.36
Na_2O	4.00	1.60	0.88	0.84
K_2O	0.36	0.27	0.13	0.16
Cl^-	19.27	10.15	9.14	8.90
Free CaO	0.15	0.86	0.67	0.60

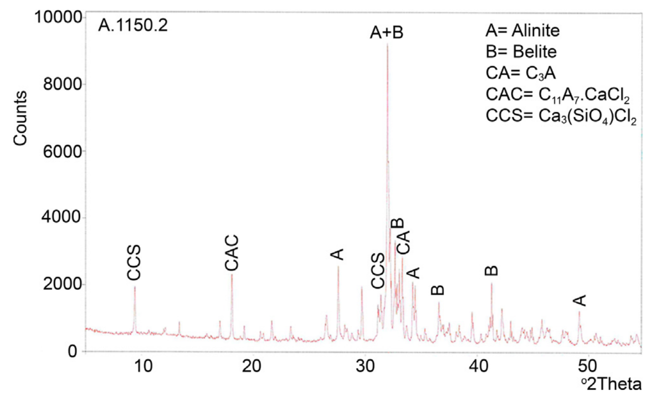

Fig. 1. XRD pattern of the alinite cement clinker calcined at 1150 °C for 2 h.

Table 4
Compressive strength of alinite cement pastes with different gypsum additions.

Sample	Compressive Strength (MPa)			
	2-Day	7-Day	28-Day	90-Day
A.1150.2 + 3% Gypsum	10.9	15.4	23.2	–
A.1150.2 + 6% Gypsum	11.7	15.9	24.2	36.6
A.1150.2 + 9% Gypsum	12.8	16.7	25.0	–
A.1150.2 + 12% Gypsum	14.7	19	29.2	39.4

2.2. Alinite cements

Preliminary trials for determining the optimum temperature and calcination time of alinite cement clinker had revealed a maximum calcination temperature of 1150 °C and the time for the maximum temperature application as 2 h to be suitable (labeled as A.1150.2). The chemical compositions of the resulting clinkers are given in Table 3.

XRD pattern of the alinite clinker is shown in Fig. 1. The main mineral phases present in the clinker were alinite, belite, trical-