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SECONDARY RESOURCES RECYCLING IN BUILDING AND REFRACTORY BINDERS TECHNOLOGY

The binders manufacture requires continuous expenditures of natural raw while there is a lack of relatively pure raw sources. Latest ten year analysis of limestone chemical content changing at the cement plants shows that limestone raw contains some impurities enabling to cause the long-time strength reducing. Thus, the traditional raw substitution along with the various industrial waste utilization problems is urgent in connection with a rising necessity to extend the raw base and to improve the ecological situation in Ukraine. Beside at the moment the million tons of waste are being accumulated and every year their amount rises.

Taking this into consideration the dolomite dust from the different processing steps of refractory production and pickle – cleaning slurry of soda and caustic production have been investigated [1]. Typical raw materials analysis is given in Table 1. The waste are adequate raw resources to make Ukraine self-sufficient with regard to the manufacture of secondary resources binders. The presence of $CaCO_3$ ($d\cdot10^{-10}$ = 1,71; 2,08; 2,27; 2,49; 3,02; 3,39; 3,84 m), $Mg(OH)_2$ ($d\cdot10^{-10}$ = 2,36; 2,30; 4,80 m), $CaAl_2O_4$ ($d\cdot10^{-10}$ = 4,67; 2,96; 2,85; 2,51; 2,01; 1,92 m), and $MgAl_2O_4$ ($d\cdot10^{-10}$ = 4,67; 2,85; 2,43; 2,02; 1,65 m) detected by X-ray analysis as the main chemical compositions of waste confirm that they are able to contribute to the hydration and strength development of refractory binders.

Table 1 – Chemical analysis ranges of waste as raw materials

Oxide constituents	Dolomite dust, %	Pickle-cleaning solid waste, %
CaO	45.42	33.71-46.72
MgO	23.32	10.02-13.37
SiO_2	4.25	-
SO_3	-	0.41-3.53
LOI*	23.11	30.87-36.77

*LOI – loss on ignition

The $CaO-Al_2O_3-MgO-SiO_2$ quaternary system studying [2] provides the basis for IWSC (industrial waste spinel cements) technology useful to the building and refractory industries. The present paper identifies the predominant $CaAl_2O_4$, Ca_2SiO_4, $MgAl_2O_4$ phases responsible for development refractory cements. Table 2 lists the eutectic compositions and temperatures estimation of pseudobinary systems. It emphasizes the ability all of these compositions to be used to refractory cements manufacture, as the Ca_2SiO_4 – $MgAl_2O_4$ compositions favor to high refractoriness cements manufacture.

Table 2 – Eutectic compositions and temperatures

Pseudobinary system	Eutectic temperature, ^0C	Composition, %	
		1st phase	2nd phase
Ca_2SiO_4 – $CaAl_2O_4$	1571	12	88
Ca_2SiO_4 – $MgAl_2O_4$	1902	48	52
$CaAl_2O_4$ – $MgAl_2O_4$	1568	87	13

The sinter process is the main method for manufacture IWSC. The proportioned (Table 3) dried at 100 ^0C raw mixes were sintered at 1350 to 1400 ^0C (with the 3-h hold at maximum temperature) into laboratory kiln, fast cooled, and then ground to cement fineness. The refractory cements synthesis technological variables have been worked out [3]. It has been recognized that optimum firing temperature range is 1350-1400 ^0C. Figure 1 supports this premise.

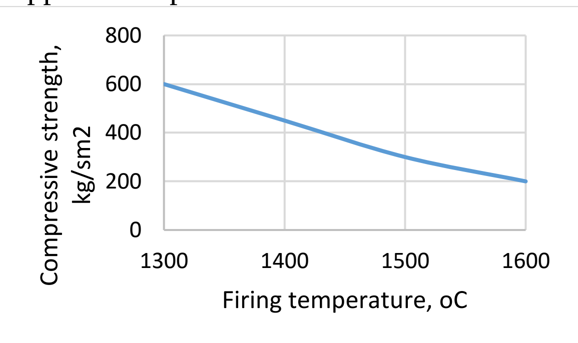

Fig. 1. Effect of firing temperatures on strength of the IWS cements

Having explored mechanical-strength and technical properties it is revealed that cements obtained are fast-hardening hydraulical binders with water-cement ratio 0,3 – 0,35; compressive strength in age 72 hours – 35 – 45 MPa and refractoriness more 1700 ^0C.

Table 3 – Typical chemical and phase compositions of IWS cements

Oxide composition, %			Phase composition, %	
CaO	MgO	Al_2O_3	$CaAl_2O_4$	$MgAl_2O_4$
44.83	11.80	43.37	80	20
26.60	7.10	66.30	75	25
24.80	8.45	66.75	70	30

By means of the physical-chemical analysis methods [4] the main phases of IWS cement clinker $CaAl_2O_4$, $CaAl_4O_7$, $MgAl_2O_4$ have been defined. High mechanical strength of cured cement stone corresponds precisely with the occurrence of complicated assemblage calcium aluminates hydraulical compounds of different base and magnesium hydrates as the colloidal as the crystalline state. The presence of magnesium spinel is providing the high service properties for cement [5].

Table 4 lists the compound constituents of IWSC according to their relative reaction rate with H_2O. They form the hydrated cement phases responsible for developing strength after curing in a humid environment. Monocalcium aluminate ($CaAl_2O_4$ or CA) is the main active ingredient in IWSC. It hydrates sufficiently fast to satisfy the short turnaround demands of industry. Fast set is prevented by restricting free lime to a low level (<0.3 C). All of these compounds react with H_2O to form the hydrated phases which provide the fundamental basis for IWSC technology [3].

Table 4 – Mineralogical phases in IWS cements

Relative hydration rate	Fast	Slow	Nonhydrating
Phases	$CaAl_2O_4$, $CaAl_4O_7$, $Ca_{12}Al_{14}O_{33}$	Ca_2SiO_3, $Ca_2Al_2SiO_7$	$MgAl_2O_4$, Al_2O_3

The remaining compounds listed in Table 4 are inert or react very slowly with H_2O at ordinary temperatures. They make an insignificant contribution to the hydration and strength development of refractory concretes, except during extended curing times.

Portland-cement concretes have limited refractory application. Unlike IWS cements, they do not retain their integrity when subjected to prolonged periods of high temperatures, cyclic heating and cooling, and other deleterious conditions of corrosion and erosion present in high temperature industrial processes. Portland-cement binders are rarely used for application above 650 ^0C and perform poorly when thermally cycled in presence of moisture to temperatures above 425^0C [6].

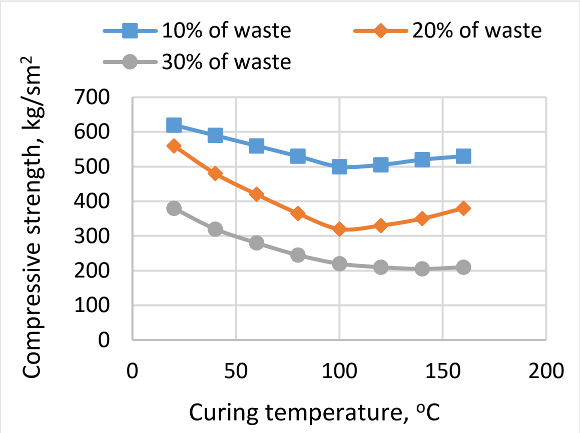

Fig. 2. Effect of curing conditions on strength of Portland-cement added with waste

The standard practices were developed to use the ability of waste to be the Portland-cement partial substitute. They require no processing prior before being ground with 70, 80 and 90% of Portland-cement to cement fineness and humidity, similar to that used in the manufacture of building materials [3]. Table 5 and Figure 2 further clarify the mechanical-strength properties of cement compositions obtained after curing and/or during steam curing. Partial substitution of cement to 10% does not reduce the mechanical-strength properties, but increasing the waste addition more 10% requires autoclave curing as the best curing conditions.

Table 5 – Comparative mechanical-strength properties

Composition	W/C ratio	Compressive strength at the curing conditions, MPa					
		Humid environment				Steaming	Autoclave
		3 days	7 days	28 days	90 days		
10% of waste 90% of PC	0.3	37	48	58	64	47	47
20% of waste 80% of PC	0.32	30	35	45	58	26	37
30% of waste 70% of PC	0.35	20	23	26	42	15	20

Developed IWS cements on the base of secondary resources are the perspective materials to manufacture more effective heat-resistant protective coatings, refractory mortars, concretes or castables linings being used in high temperature processing units.

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