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UTILIZATION OF HEAT POWER INDUSTRY WASTE IN THE FORM OF BINDING COMPOSITE MATERIALS IN KYRGYZSTAN

Abstract. This paper discusses the urgent problem of expanding the raw material base of the construction industry using fuel slags in cements. The influence of various methods of preparation and introduction of fuel slags on the basic properties of composite cementing materials was evaluated. It is shown how the properties of the composite cement-slag binder vary depending on the application method and the activation degree of the slag.

Key words: technogenic raw material; ash and slag mix; mixing; grinding; composite binding material; glass phase; hydraulic activity; chemical and mineralogical composition; dispersability; water demand; strength.

One of the research priorities in the development of the Kyrgyz Republic is the rational use of natural resources.

For the construction industry, the most promising resource and energy saving solution is the integrated use of affordable, cheap local raw materials, which include industrial waste such as ash and slag of thermal power plants that are in huge quantities accumulated in dumps, causing significant damage to the environment.

If the use of ash and slag wastes (ASW) in the developed countries is 50-90%, in Central Asian countries this figure is less than 4%.

In the city of Bishkek a huge stockpiling of ash and slag wastes, as well as wet ash discharge, fly ash and sulfogypsum were accumulated, which are formed as a result of desulfurization of flue gases. Utilization of waste from thermal power plants is of considerable interest both in solving the environmental problem and for the economic efficiency of the enterprise.

The research aim: development of gypsum binders from waste from Bishkek TPP.

Materials and methods. Sulfogypsum, which is formed as a result of desulfurization of flue gases, is characterized by a specific surface area (S = 2800-3000 cm^2/g); by the content of $CaSO_4 \cdot 2H_2O$ – 93-95%; $CaCO_3$ – 1.6-1.7%; pH 4.5-9; ρ_{bulk} – 520-530кг/м^3; ρ_{true} – 2.35-2.37 g/cm^3; W = 20-27%. It can be attributed to high-quality gypsum raw materials of Class I and the production of gypsum binders on their basis is of undoubted interest.

The chemical composition of the HPP waste is given in the table 1.

Table 1 – Chemical composition of raw materials

No.	Oxide content, %									
	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	SO_3	Na_2O	K_2O	П.п.п.
Sulfogypsum	0.09	0.23	0.36		55.72	0.76	0.07	–	–	41.55
Fly ash	55.4	23.15	4.30		2.18	1.35	1.08	1.72	2.08	4.94
Wet ash discharge	52.0	21.58	0.97	0.97	6.47	1.14	0.21	0.9	1.7	12.13
Cement of KCSP	22.44	4.65	4.11		65.59	1.75	0.33	–	–	0.2
Sand from Vassiliyevskiy	68.72	14.21	3.24		3.25	2.68	2.61	–	–	

The laboratory of Kyrgyz State N. Issanov University of construction, transport and architecture obtained the construction gypsum based on sulfogypsum. Gypsum was cooked at a temperature of 150 °C with an exposure time of 90 minutes at the indicated temperature; time of temperature rise - 40 min.

The test of construction gypsum was carried out in accordance with GOST (National Standards) 23789-79. According to physical and mechanical properties, the construction gypsum from sulfogypsum corresponds to grade G-4-B-III (table 2).

Table 2 – Physical and mechanical properties of the construction gypsum from sulfogypsum

Temperature of burning, °C	Grinding fineness 02, %	Standard consistency, %	Setting time, min		Sample density, g/cm³	Strength limit after 2 hours in MPa	
			start	end		R_{flex}	R_{rupt}
150	0	68	12	16	1.64	1.86	4.2

Since the construction gypsum based on sulfogypsum has a low resistance to environmental influences and a sharp decrease in strength in moistening, the fillers and additives were modified to improve the water resistance of gypsum binders. As a basic component of the binder, G-4 gypsum, obtained from sulfogypsum, was used.

Ash of Bishkek TPP with a specific surface of S_{spec} = 350-400 m^2/kg was used as a filler in gypsum binders. They have pozzolanic activity as they contain clay-firing products: amorphous clayey material such as metakaolinite, amorphous SiO_2, Al_2O_3, Fe_2O_3 and aluminosilicate glass. High hydraulic activity of the amorphous clay substance is associated with its high specific surface, which is created as a result of the decomposition ($Al_2O_3 \cdot 2SiO_2$) into amorphous alumina and silica.

The thermally treated quartz which is contained in the ash, due to increased solubility, interacts with calcium hydroxide. The higher the concentration of hydroxide in the liquid phase is, the more active the ash is.

According to the characteristics of the ash activity modulus M_0 = CaO+MgO/SiO_2+Al_2O_3 = 0.045, the alumina module p = Al_2O_3/Fe_2O_3, the modulus of activity M_a = Al_2O_3/SiO_2 = 0.41, it can be inferred that for $M_0<1$, the ash has increased activity. In this case, the higher the activity modulus is, the faster the ash hardens in the grinded state. An important feature of ash is its high intensive grinding capacity.

Lime of the 1st grade and portland cement were used to activate low-calcium acid ash. Lime is characterized by the content of CaO+MgO within 92% and the content of unhydrated, unslaked particles is 0.5%.

The addition of K_2SO_4 together with lime in the composition of the binder causes high concentrations of potassium and sulfate ions. Calcium sulphate and potassium sulfate can be isolated as a double salt, as a result of recrystallization of which the spatial structure of $CaSO_4 \cdot 2H_2O$ is formed. Phase transformations of crystalline hydrate new-growths stimulate a change in the kinetics of expansion of the system and a general decrease in deformation.

Research findings and their discussion. During the research, a 4-factor experiment was carried out according to the B_4 plan, consisting of 24 experimental points. Each of the prescription factors performs a certain role in the formation of the structure of the gypsum binder and changed at three levels: X_1 - ash (0..15 ... 30%); X_2-lime (0 ... 2 ... 4%); X_3-K_2SO_4 (0 ... 1.5 ... 3.0%); X_4-cement (0 ... 5 ... 10%); the rest is gypsum-waste of TPP.

As the main parameters of gypsum binder are selected: Y_1 - Normal thickness, Y_2 initial setting period, min .; %; Y_3 - end of setting, min .; Y_4 - R_{bend}., MPa; Y_5 - $R_{compres}$., MPa; Y_6-$R_{compress.\ of\ wet}$, MPa; the softening factor is Y_7.

Optimization criteria Kp ≥ 0,6 and strength $R_{dry\ compres} \geq 10$ MPa.

Table 4 – Experiment plan B_4

No.	Encoded variables				Experiment results							
	x_1	x_2	x_3	x_4	Y_1 НГ, %	Y_2 Average setting start (min)	Y_3 Average set end:min	Y_4 $R_{bend.}$ MPa	Y_5 $R_{dry\ compr}$ MPa	Y_6 $R_{wet\ compr.}$ MPa	Y_7 K_p	Y_8 W, %
1	+	+	+	+	68	6.21	7.75	1.13	5.68	2.89	0.51	34.5
2	+	+	+	–	65	6.33	8.0	1.25	5.76	2.76	0.48	37.9
3	+	+	–	+	67	14.55	20.25	1.67	6.88	3.50	0.51	36.9
4	+	+	–	–	67	19.75	29.25	1.97	5.88	2.64	0.45	38.8
5	+	–	+	+	70	2.81	3.60	1.37	5.28	2.48	0.47	42.2
6	+	–	+	–	68	2.25	2.83	1.33	5.12	1.28	0.25	43.9
7	+	–	–	+	67	10.16	17.58	2.55	7.68	4.37	0.57	31.0
8	+	–	–	–	67	10.75	19.16	2.47	7.0	3.92	0.56	30.8
9	+	+	+	+	67	5.75	7.41	2.51	10.52	5.04	0.48	34.9
10	–	+	+	–	68	5.75	7.48	2.16	8.72	3.31	0.38	34.9
11	–	+	–	+	70	15.16	19.50	2.8	10.26	4.51	0.44	38.2
12	–	+	–	–	67	13.50	19.91	2.93	13.24	6.22	0.47	35.4
13	–	–	+	+	67	2.08	3.58	2.45	10.44	5.01	0.48	35.5
14	+	–	+	–	65	2.20	2.95	2.65	8.84	4.98	0.46	43.1
15	–	–	–	+	63	8.83	15.08	3.32	10.7	6.54	0.61	33.8
16	–	–	–	–	60	12.66	18.83	2.81	8.56	4.24	0.48	39.6
17	+	**0**	**0**	**0**	70	4.83	8.75	1.69	8.6	5.16	0.6	32.3
18	–	**0**	**0**	**0**	62	6.50	11.10	2.64	10.32	5.26	0.51	34.0
19	**0**	+	**0**	**0**	63	8.86	13.93	1.84	8.88	4.97	0.56	36.8
20	**0**	–	**0**	**0**	63	3.25	4.58	2.35	22.8	14.82	0.65	34.2
21	**0**	**0**	+	**0**	68	5.03	6.11	1.9	8.68	5.2	0.60	35.9
22	**0**	**0**	–	**0**	70	14.08	22.18	2.65	8.72	5.23	0.60	40.6
23	**0**	**0**	**0**	+	68	6.86	8.58	2.28	10.12	6.27	0.62	39.5
24	**0**	**0**	**0**	–	67	6.83	8.33	2.29	11.0	6.71	0.61	32.3

Based on the results of the experiment, specifying the average error S and significance level $\alpha = 0.01$, the mathematical models of the properties of the gypsum binder were obtained.

***Y_2* - Start of the setting, min.**

$$(Y_2) = 6.48 + 0.29\,x_1 - 0.82x_1^2 + 0.41x_1x_2 - 0.20x_1x_3 - 0.19\,x_1x_4 + 2.27\,x_2 - 0.43x_2^2 - 0.37x_2x_3 - 0.02\,x_2x_4 - 4.502\,x_3 + 3.072\,x_3^2 + 0.517\,x_3x_4 - 0.423\,x_4 + 0.362\,x_4^2 \quad (1)$$

***Y_3* - End of setting, min.**

$$(Y_3) = 9.694 + 0.629\,x_1 + 0.231\,x_1^2 + 0.514\,x_1x_2 - 0.76\,x_1x_3 - 0.404\,x_1x_4 + 2.516\,x_2 - 0.39\,x_2^2 - 0.036\,x_2x_3 - 0.363\,x_2x_4 - 7.335\,x_3 + 4.451\,x_3^2 + 0.989\,x_3x_4 - 0.745\,x_4 - 1.239\,x_4^2 \quad (2)$$

***Y_4* - *$R_{bend.}$* Bending resistance, MPa**

$$(Y_4) = 2.209 + 0.491x_1 - 0.054x_1x_2 - 0.093\,x_1x_3 - 0.052x_1x_4 - 0.0169x_2 + 0.064x_2x_3 - 0.357x_3 - 0.006\,x_3x_4 \quad (3)$$

Y_5-$R_{dry\ compr.}$ MPa

$$
\begin{aligned}
(Y_5) = {} & 12.133 - 1.873\, x_1 - 2.673\, x_1^2 - 0.317\, x_1x_2 - 0.085x_1x_3 - 0.05\, x_1x_4 \\
& - 0.589\, x_2 + 3.707\, x_2^2 - 0.082x_2x_3 - 0.302\, x_2x_4 \\
& - 0.549\, x_3 - 3.433\, x_3^2 + 0.165\, x_3x_4 \\
& + 0.191\, x_4 - 1.573x_4^2
\end{aligned} \quad (4)
$$

Y_7-K_{soft} - softening factor

$$
\begin{aligned}
(Y_7) = {} & 0.633 + 0.005\, x_1 - 0.078\, x_1^2 + 0.022\, x_1x_2 - 0.011\, x_1x_3 + 0.006\, x_1x_4 \\
& - 0.014\, x_2 - 0.028\, x_2^2 + 0.034\, x_2x_3 - 0.014\, x_2x_4 \\
& - 0.032\, x_3 - 0.033\, x_3^2 + 0.012\, x_3x_4 \\
& + 0.031\, x_4 - 0.018\, x_4^2
\end{aligned} \quad (5)
$$

A preliminary analysis of the ES coefficients of the models (1, 2) of the setting time of the composite gypsum binder showed that the setting time is significantly accelerated with the addition of K_2SO_4, which indicates the crystallization effect. So for model (1) the setting start, the linear coefficient at factor x_3 was $b_3 = -4.502$. For the model (2), the end-of-setting, the linear effect is $b_3 = -7.335$.

Linear effects at the factor x_2 (lime) indicate an increase at the staart and end of the setting of the gypsum binder. For the model (1), $b_2 = + 2.271$, and for the model (2) $b_2 = + 2.516$, because lime reduces the solubility of gypsum, thereby prolonging the setting time.

The presence of ash (x_1) and cement (x_4) does not significantly affect the setting time of the gypsum binder ($b_1 = 0.289$ and $b_4 = -0.423$) and ($b_1 = 0.629$ and $b_4 = -0.745$).

Analysis of flexural and compressive strength models of gypsum binder (3, 4) showed that the presence of ash (x_1) and cement (x_4) should be at the optimal level ($b_{11} = -2.673$) and ($b_{44} = -1.573$). Their maximum content leads to a large utilization of ash, but results in a decrease in the strength of the binder. Increasing the amount of cement is not advisable, because it increases the amount of ettringite, which is formed during the hydration of cement. The content of lime additives (x_2) and K_2SO_4(x_3) should be optimized, as can be seen from the quadratic effects (b_{22} =3.707 и b_{33} = -3.433).

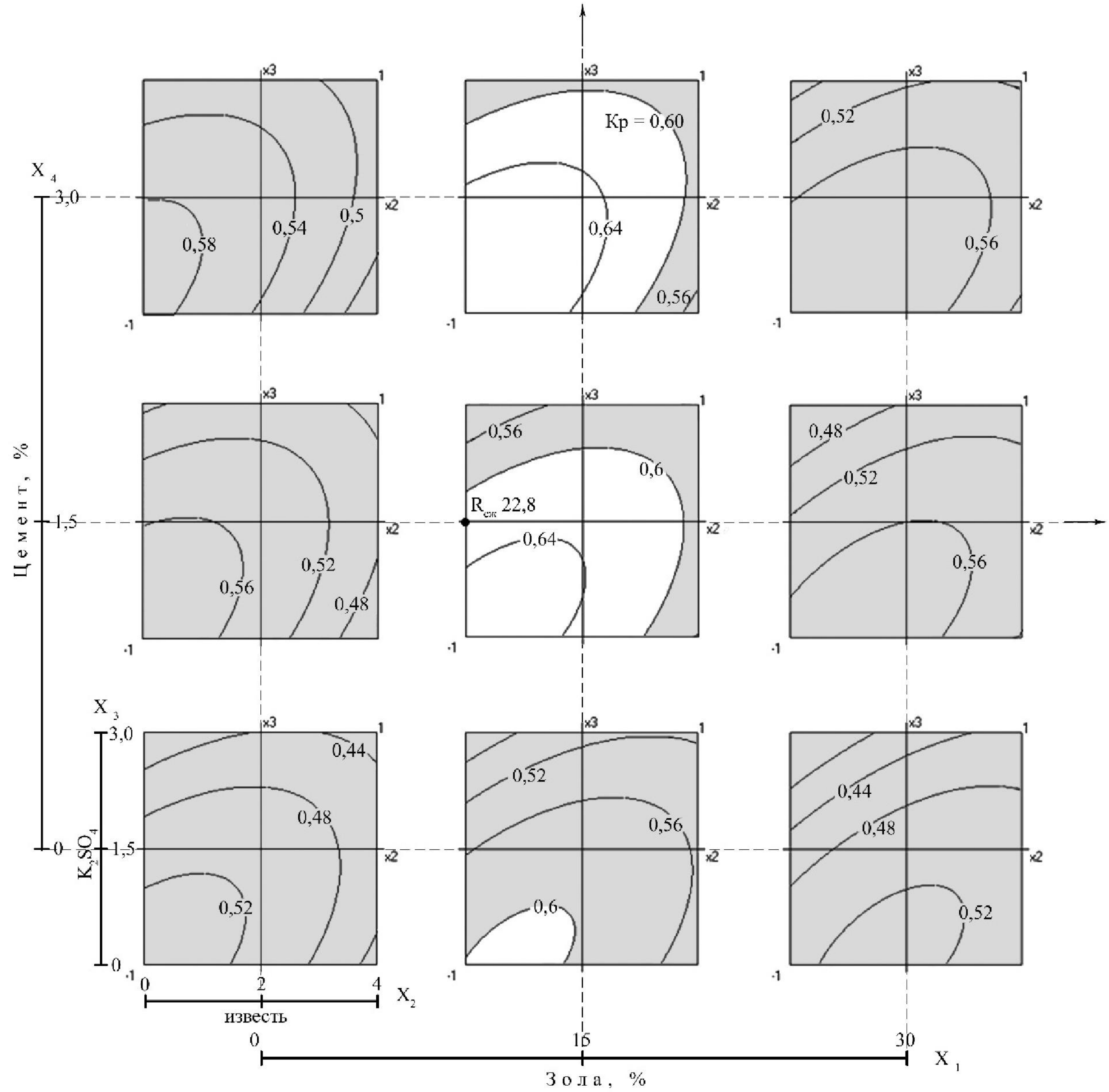
The Ks_{oft} factor of the softening agent (Y_7) of the gypsum binder is within the permissible range of $Ks_{oft} \geq 0.6$, provided that there is an ash additive ($b_1 = 0.005$), but in the optimal amount ($b_{11} = -0.078$). This fact shows the formation of insoluble compounds, as a result of the interaction of ash with calcium hydroxide, which contribute to an increase in water resistance. The optimal cement content also provides ($b_{44} = -0.018$) an increase in the water resistance of the gypsum binder ($b_4 = + 0.031$). To ensure the required K_{soft}, the lime (x_2) and K_2SO_4 (x_3) content is a prerequisite and depends on the amount of ash ($b_{12} = 0.022$, $b_{13} = -0.011$, $b_{14} = + 0.006$).

The softening coefficient of samples from gypsum as seen from the results of the experiment for all points of the plan varies between $0.25 \leq K_{soft} \leq 0.65$. According to the optimization conditions, $K_{soft} > 0.6$ is achieved if the optimum formulation of the constituent components is fulfilled: the amount of ash X_1 = 15%, lime X_2 = 1.5 ... 2%, $K_2SO_4X_3$ = 1 ... 1.5%, cement X_4 = 1.5 ... 3.0%.

In figure, it is clearly possible to observe an area where an increased value of the coefficient $K_{soft} > 0.6$ (an unpainted zone) is provided. Here it is necessary to adhere to the formula mentioned above.

Thus, studies have shown the utilization possibility of the ash in gypsum binders while maintaining the required quality indicators. Moreover, with the optimal amount of additive components, the strength characteristics and the softening factor increase.

To obtain waterproof gypsum binders with $K_{soft} \geq 0.6$ and strength $R_{dry\ compr.}$.≥ 10 MPa, the following formula is recommended: fly ash 15 ... 22%; lime1.5 ... 2%; cement 1.5% and K_2SO_4 1.5%.



The isolines of the softening coefficient of samples from gypsum $Y_7(K_{soft}) = f(x_2, x_3)$ in nine points of the factor space x_1 and x_4

Conclusion:

- Sulphogypsum was obtained at the Bishkek TPP by desulfurizing industrial gases, which can be attributed to gypsum raw materials of grade I;
- Construction gypsum G4-B-III was obtained on the basis of sulfogypsum;
- To increase the water resistance of gypsum binders the experimental-statistical modeling has been conducted which revealed that the use of fly ash as a filler together with lime and K_2SO_4 promotes the regulation of the setting time (elongation), which is important in the technological plan. Growth of the K_{soft} and of the water absorption of gypsum stone shows an increase in water resistance of gypsum products due to the formation of insoluble hydrosilicates in the process of hydration of ash and clinker minerals of cement with lime.
- Waterproof modified gypsum binders can find application for the manufacture of products for various purposes.
- Within the framework of one enterprise, ash and sulfogypsum are recycled, which is economically feasible.

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ҚЫРҒЫЗСТАННЫҢ ЖЫЛУ ЭНЕРГЕТИКАСЫНЫҢ ҚАЛДЫҚТАРЫН КОМПОЗИЦИЯЛЫҚ БАЙЛАНЫСТЫРҒЫШ ЗАТТАРДА ПАЙДАЛАНУ

Аннотация. Мақалада цементтердегі отын шлактарын пайдалана отырып, құрылыс индустриясының шикізат базасын кеңейтудің өзекті мәселесі туралы айтылады. Композициялық байланыстырғыштардың негізгі сипаттарына отын шлактарын дайындау және енгізу түрлерінің тәсілдеріне баға жасалды. Шлакты енгізу тәсілі мен белсендіру дәрежесіне қарай композициялық цементті-шлакты байланыстырғыштың сипатының қалай өзгеретіндігі анықталды.

Түйін сөздер: техногендік шикізат; күл қоспасы; араластыру; ұсақтау; композициялық байланыстырғыш; шыны фазасы; гидравликалық белсенділік; химиялық-минералдық құрам; дисперсия, су сұранысы, төзімділік.

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ИСПОЛЬЗОВАНИЕ ОТХОДОВ ТЕПЛОЭНЕРГЕТИКИ КЫРГЫЗСТАНА В КОМПОЗИЦИОННЫХ ВЯЖУЩИХ ВЕЩЕСТВАХ

Аннотация. Статья посвящена актуальной проблеме расширения сырьевой базы строительной индустрии за счет использования топливных шлаков в цементах. Проведена оценка влияния различных способов подготовки и введения топливных шлаков на основные свойства композиционных вяжущих. Показано как изменяются свойства композиционного цементно-шлакового вяжущего в зависимости от способа введения и степени активизации шлака.

Ключевые слова: техногенное сырье; золошолаковая смесь; смешение; измельчение; композиционное вяжущее; стеклофаза; гидравлическая активность; химико-минералогический состав; дисперсность, водопотребность, прочность.

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