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Study of complex processing of 10-160 mm grade chromium tailings by encapsulation in GreenCrete™ composite sulfur concrete

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Abstract. In recent years, methods of utilization of lumpy mineral raw materials of chromium production by encapsulation with modified sulfur from substandard grades of oil to obtain sulfur concrete have become increasingly popular. A significant amount of lumpy waste with a low content of Cr_2O_3 (~ 5-7% w/w) is formed when Kazakhstani chrome raw materials are processed by gravitation methods, and they can only be used as backfill in mine construction or as a component in building and road-building mixtures. Wastes from chromium deposits in Kazakhstan are located in close proximity to oil deposits in the Aktobe region, which are characterized by a high content of sulfur-containing heavy oils, which can be jointly disposed of in the form of sulfur concrete. Composite material - sulfur concrete is produced based on sulfur polymer binder - GreenCrete™ modified sulfur under GOST R 56249-2014. The possibilities of the sulfur-concrete composite formation process for the use of beneficiation tails of 10-160 mm class chromium raw material as inert materials have been studied. The characteristics of the samples obtained during the tests allow us to draw conclusions about the relatively successful encapsulation of chromium production waste in an amount of 15% by weight of the sample with the formation of sulfur concrete of the M400 class, while with a 10% content of materials for enrichment of chromium raw materials, the M500 indicator was achieved.

Keywords: *chromium raw materials, mine backfill, road pavement, sulfur polymer binder, recycling of poor chromium raw materials.*

1. Introduction

The problem of disposal of chrome ore tailings, a toxic waste from chrome ore processing, has not been solved anywhere in the world so far resulted in closure of chrome production in a number of developed European countries and Japan [1]. In particular, the high content of calcium and silicon in the sludge prevents its use in the production of refractory materials.

The mines and quarry of the Donskoy GOK are located near the city of Khromtau in the northwestern part of Kazakhstan, 90 km east of Aktobe, the administrative centre of the Aktobe region. There are currently two mines and a quarry, two processing plants and two tailings processing sites in operation. At the concentrating plant, a large-sized chromium concentrate is obtained by heavy-medium separation with a Cr_2O_3 content of 48-50%, which is melted in electric arc furnaces to obtain ferrochrome [2]. Currently, poor chromite ores and dumps of off-balance ores are involved in processing, which serves as additional sources of raw materials. When they are enriched, large-sized fragments with a low chromium content remain in the waste rock.

In recent decades, increasing volumes of oil and gas production, as well as deep cleaning of oil and gas from sulfur, have led to the storage and accumulation of vast reserves of sulfur. One of the promising ways to sell these sulfur reserves is the production of compositions based on sulfur (sulfur concrete, sulfur asphalt concrete). The main advantages of sulfur concrete over ordinary concrete are its higher strength characteristics (in compression and bending), low water absorption, the ability of this material to work in tension, corrosion resistance, water resistance, frost resistance, rapid strength development, low shrinkage and the possibility of recycling. At the same time, concrete and sulfur concrete are approximately equal in cost. But the production of sulfur concrete is possible even on fine sands (ordinary concrete will fall apart on such sand or require enormous overspending of the binder). And if traditional concretes are at least three-component, then sulfur concrete consists of two: modified sulfur and any of the fillers. However, the properties of sulfur concrete depend on the exact observance and control of the technological process and quality control of the input raw materials at all stages of production.

Sufficiently high content of Mg^{2+}, Al^{3+}, Fe^{3+} Mg^{2+}, Al^{3+} and Fe^{3+} ions in the initial chromium raw material prevents the formation of a compound - elite - the main component of cement- three-calcium silicate (Ca_3SiO_5), when, as in the production of sulfur concrete, such a problem no longer exists. However, the properties of sulfur concrete depend on the exact observance and control of the technological process and the quality control of incoming raw materials at all stages of production.

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er). And if traditional concretes are at least three-component, then sulfur concrete consists of two: modified sulfur and any of the fillers. Reinforced concrete piles, foundation blocks, railway sleepers, road and paving slabs, curbstones, weights for gas and oil pipelines, sewer and water wells, hatches for heating mains, etc. can be made from sulfur concrete; monolithic foundations and pavements of roads and sites; hydraulic structures, including facing slabs for irrigation canals and construction, slabs for the construction of hydroelectric power stations, state district power plants and other hydraulic construction, bank protection, breakwaters; underground storage facilities for the disposal of aggressive environments, including radioactive ones, and much more [3].

When testing the sulfur asphalt concrete pavement, resistance to mechanical loads and weather and climatic conditions was shown. In sulfur-asphalt concrete, sulfur plays the role of a binder between bitumen and crushed stone, and has high adhesive properties with positively and negatively charged microparticles of the crushed stone grain surface, due to which the adhesion properties between bitumen and crushed stone increase. Couplings pass through the entire geometry of the cleavage, and not through particles of the same charge. Therefore, new composites do not require the use of surfactants. In the era of the emergence of higher axial loads and a high increase in traffic intensity, modern road surfaces should provide increased shear resistance at high summer temperatures, crack resistance at low temperatures, and be characterized by high corrosion resistance under the influence of anti-icing materials (chemical reagents). At the same time, a due role in assessing the durability of road surfaces is given to wear resistance, the ability of the material to withstand the effects of heavy traffic at high speeds, as well as the effects of studded tires and various other factors. The increase in the functional reliability of asphalt concrete pavements is currently associated in the world with the use of various modifying additives that help improve the transport and operational properties of road pavements. Such modifiers include: polymeric thermoplastic elastomers, crumb rubber and others. Bitumens of different viscosities and bituminous mastics are used as a binder. Therefore, the duality of sulfur is considered as a copolymer binder and as a reinforcing component that creates the effect of a “stone flower” [4–9]. In sulfur-asphalt concrete, sulfur plays the role of a binder between bitumen and crushed stone, has high adhesive properties with positively and negatively charged microparticles of the crushed stone grain surface, due to which the adhesion properties between bitumen and crushed stone increase. Couplings pass through the entire geometry of the cleavage, and not through particles of the same charge. Therefore, new composites do not require the use of surfactants (surfactants, high adhesion to stone material).

In a number of countries (Russia, USA, Canada, France, England, Holland) there is a wide experience in the use of sulfur in the manufacture of concrete (sulfur concrete), as mentioned above, and asphalt coating (sulfur bitumen), in order to reduce cracking, increase thermal stability, save up to 50% organic binder component [10].

Sulfur-containing road surfaces help to reduce the consumption of bitumen, which in turn is a valuable oil-bearing raw material and belongs to super-heavy grades of oil. The addition of sulfur makes it possible to improve the performance of the pavement in compression, respectively, to reduce the functional thickness of the pavement and to reduce the consumption of gravel by a factor of three. Such pavements have a longer service life, do not crack in the heat and cold, and have a higher resistance to dynamic loads. Sulfur is actively used in road construction in Canada, USA, EU. High performance road surfaces contain up to 40% sulfur. It has been proven that sulfur asphalt is safe after curing. At the same time, it is estimated that the use of sulfur in the construction of roads will significantly reduce their cost by reducing the thickness of the coating, the amount of bitumen and gravel used. Also, the cost of maintaining roads will be reduced due to the use of a more efficient and wear-resistant coating [11].

It is possible to form binder components from the mineral part of chromite raw materials based on compounds similar in chemical composition to Sorel cements but it requires the use of additional chemical compounds [12-15].

The production of composite sulfur concrete is connected with the use of a binder with a different nature - modified sulfur with a proportion of "insoluble sulfur" of a metastable polymeric modification requiredunder GOST R 56249-2014. Chemisorption processes involving metastable polymer modification with the formation of a solid composite material - sulfur concrete take place at elevated (up to 150°C) temperatures and the interaction with silicon oxide sand. Industrial wastes in this case serves as an inert filler performing a structuring function in the amount of the rocky body [16-17].

Green Crete modified sulfur under GOST R 56249-2014 (modified technical sulfur for the sulfur concrete production) is a product of processing lump or liquid Claus block sulfur under conditions of chemical conversion. Technically, there are now no restrictions on the performance of such equipment supplying a binder for the sulfur concrete production process. Modular sulfur-concrete plant provides isothermal mixing of modified sulfur with inert materials in a mass ratio of 1:3 with the capacity of 20 tons/hour and more, with the production of commodity sulfur-concrete, under PNST 105-2016, and reinforced concrete products based on it.However, these technologies are not widely used in Kazakhstani industries, so this work is relevant and significant for the concrete industry.

2. Methods

The studies were performed to obtain comparative characteristics of the physical and operational characteristics of the sulfur concrete samples in comparison with Portland cement concrete.

Physical and performance properties of the sulfur concrete samples obtained in comparison with Portland cement concrete are presented in Table 1 and depend on inert fillers: crushed stone and fine-dispersed admixtures, as well as on the efficiency of air removal from the amount of material in a concrete mixer.

Normative document PNST 105-2016 provides the following classification of inert materials:

1. Use as a fine filler - use the products obtained by grinding of rocks or solid industrial waste to prepare sulfur concretes. Acid resistance of fine aggregate must not be less than 97%.
2. Use sand under GOST 8736 as the fine aggregate for sulfur concrete. Acid resistance must be not less than 97%.
3. Use crushed rock or crushed gravel under GOST 8267, slag crushed under GOST 3344 as the coarse aggregate for heavy sulfur concretes. The maximum grain size of the aggregate must be not more than 40 mm.

Table 1. Comparative characteristics of GreenCrete sulfur concrete and Portland cement concrete

Parameters	Unit of measurement	Modified sulfur concretes		Portland cement concrete
		With dense aggregates	With porous aggregates	With dense aggregates
Average density	kg/m^3	2,300-2,500	1,600-2,000	2,200-2,400
Compression strength	MPa	40-90	30-50	30-50
Bending strength	MPa	10-12	7-8	8-10
Compression elasticity modulus	MPa	(3.5-4. 1)x1 0^4	(2-2.5)x 1 0^4	(2.4~2.8)x10^4
Poisson's ratio	-	0.25	0.31-0.21	0.19-0.21
Coefficient of Linear Thermal Expansion CLTE	C	(11-13)x10-^{6}	(7-9)x10-^{6}	(10-12)x10-^{6}
Linear shrinkage	%	0.02	-	0.02
Water absorption	%	0.9-1.5	0.7-1.1	1.0-3.5
Frost resistance	Cycles	300-800	up 100	100-300
Water resistance		20-40	10-20	8-10
Friction resistance	g\cm	0.4-0.45	0.3-0.35	0.35-0;4
Heat resistance	C	80	80	120
Concreting at subzero temperatures		Possible		Warmingup is required
Concreting under water, including sea water		Possible		Obstructed
Chemical resistance		High		Protectionis required
Production wastes, after operational period		Absent		Available

To prepare a sample of GreenCrete™ grade sulfur concrete, chromium raw material jigging tailings of the Donskoy Mining and Processing Plant of the 10-30 mm class have been produced, that is, they are superior in size to sand of increased size according to GOST 8736. Industrial waste samples in the amount of 10 and 15% of the final mixture weight were heated with river sand of medium coarseness and mixed with GreenCrete ™ modified sulfur (under GOST R 56249-2014 with the characteristics presented in Table 2) in the amount of 25% of the final mixture weight.

Table 2. Characteristics of GreenCrete modified sulfur

Parameter	Value
Mass fraction of sulfur, %, min.	98.80
Mass fraction of ash, %, max	1.00
Mass fraction of acids, %, max	0.02
Mass fraction of organic stabilizer, %, max.	0.20
Mass fraction of water, %, max	0.06
Mass fraction of insoluble (toluene, 60°C) part, %, min	8.00

The results of chromium waste encapsulation (The concrete is made at 150°C, the concrete hardens when it is cooled in natural conditions) are shown in Table 3.

Table 3. The results of chromium waste encapsulation

Lab number	Design concrete grade	Date of placing	Test Date
441/1,yellow	B30	13.08.2021	15.08.2021
441/2, grey	B40	13.08.2021	15.08.2021
Age, days	Strength of concrete, MPa, Rm	Required strength of concrete at the age of 28 days, MPa, Rm	Percentage of required strength
2	38.0	38.4	99
2	51.8	51.2	101

3. Discussion

Both samples of gray and yellow material, respectively, were obtained at a temperature of 150°C and in the process of intensive mixing; they were poured into 100x100 mm test cubes and vibrated on a SMZh-539 vibrating pad.

The characteristics of the samples obtained during the tests and shown in Table 3 suggest that the encapsulation of chromium production wastes in the amount of 15% of the sample weight with the production of M400 class sulfur concrete was relatively successful, while M500 was achieved at 10% of the amount of chrome beneficiation materials.

If weighting agents (e.g., lead shot) are added to the obtained sample materials it is possible to obtain composite concretes with radiation and protective properties for disposal of radiochemical wastes of low and medium activity.

The use of technical sulfur modified with additives as a binder for the production of sulfur concrete will make it possible to control its physical and mechanical properties in a wide range. In the process of preparing concrete, sulfur melts and plays the role of an independent binder, evenly distributed among the mineral components, enveloping them, creating structural bonds of the crystallization type.

4. Conclusions

The results obtained prove that the weight of the disposed chrome tails by the encapsulation method of the 10-40 mm chrome beneficiation tailings will make 24 thousand tons/year with the output of M400 class sulfur-concrete with the productivity of the experimental modular sulfur-concrete plant of 20 t/h, i.e. 160 thousand tons/year. Larger particles of the chrome beneficiation tailings must be subjected to crushing to the limit size of crushed stone specified in PNST 105-2016 for the production of sulfur concrete, i.e. 40 mm.

The number of disposed tailings can rise by increasing the productivity of the pilot plant and the number of pilot plants. The technology provides 100% replacement of Portland cement and solves the environmental problems of oil-producing regions and chromium production in Kazakhstan through using industrial waste (lump sulfur) and sludge tailings.

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GreenCrete™ маркалы композиттік серобетонға капсулалау әдісімен 10-160 мм класты хром шикізатын байыту қалдықтарын кешенді қайта өңдеуді зерттеу

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Аңдатпа. Соңғы жылдары серобетондарды алу үшін кондиционерленбеген мұнай сорттарынан модификацияланған күкіртпен капсулалау арқылы хром өндірісінің кесек минералды шикізатын кәдеге жарату тәсілдері барған сайын танымал бола бастады. Қазақстандық хром шикізатын гравитация әдістерімен өңдеу кезінде құрамында Cr_2O_3 мөлшері төмен ірі кесек қалдықтардың едәуір көлемі түзіледі (~5-7% салмақ.), олар негізінен шахта құрылысында қайта толтыру немесе құрылыс және жол-құрылыс қоспаларында компонент ретінде пайдаланылуы мүмкін. Қазақстанның хром кен орындарының қалдықтары Ақтөбе облысындағы күкірті бар ауыр мұнай сорттарының жоғары құрамымен сипатталатын мұнай кен орындарына тікелей жақын орналасқан, оларды серобетон түрінде бірлесіп кәдеге жаратуға болады. Композиттік материал серобетон МЕМСТ Р 56249-2014 стандарты бойынша GreenCrete™ маркалы модификацияланған күкірт-серополимерлі тұтқыр зат негізінде өндіріледі. Инертті материалдар ретінде 10-160 мм класты хром шикізатын байыту қалдықтарын пайдалану үшін серобетон композит қалыптастыру процесінің мүмкіндіктері зерттелді. Сынақтар барысында алынған үлгілердің сипаттамалары М400 класты серобетонды үйрете отырып, үлгі массасының 15% мөлшерінде хром өндірісі қалдықтарын салыстырмалы түрде сәтті капсулалау туралы қорытынды жасауға мүмкіндік береді, ал хром шикізатын байыту материалдарының 10% құрамында М500 көрсеткішіне қол жеткізілді.

Негізгі сөздер: *хром шикізаты, шахталық толтыру, жол жамылғысы, серополимерлі тұтқыр зат, кедей хром шикізатын кәдеге жарату.*

Исследования комплексной переработки хвостов обогащения хромового сырья класса 10-160 мм методом капсулирования в композитный серобетон марки GreenCrete™

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Аннотация. В последние годы все большую популярность находят способы утилизации кускового минерального сырья хромового производства капсулированием с модифицированной серой из некондиционных сортов нефти для получения серобетонов. При переработке казахстанского хромового сырья методами гравитации образуется значительный объем крупнокусковых отходов с низким содержанием Cr_2O_3 (~5-7 % вес.), которые могут быть использованы в основном в виде обратной засыпки в шахтном строительстве или компонента в строительных и дорожно-строительных смесях. Отходы хромовых месторождений Казахстана расположены в непосредственной близости к нефтяным залежам в Актюбинской области, характеризующимся высоким содержанием серосодержащих тяжелых сортов нефти, которые могут быть совместно утилизированы в форме серобетонов. Композитный материал серобетон производится на основе серополимерного вяжущего – модифицированной серы марки GreenCrete™ по стандарту ГОСТ Р 56249-2014. Исследованы возможности процесса образования серобетонного композита для использования хвостов обогащения хромового сырья класса 10-160 мм в качестве инертных материалов. Характеристики полученных в ходе испытаний образцов позволяют сделать выводы об относительно успешном капсулировании отходов хромового производства в количестве 15 % от массы образца с поучением серобетона класса М400, в то время как при 10 % содержании материалов обогащения хромового сырья был достигнут показатель М500.

Ключевые слова: *хромовое сырье, шахтная засыпка, дорожное покрытие, серополимерное вяжущее, утилизация бедного хромового сырья.*