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Article

Concretes based on technogenic wastes formed during the mechanical processing of carbonate rocks

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Abstract. This article considers the possibility of using technogenic waste from the mechanical processing of Sastobe carbonate rocks as coarse and fine aggregates in the production of heavy concrete. X-ray diffractometric analysis $CaCO_3$ d = (3.849-3.14-2.49-2.277-2.088-1.912-1.869 A^0) and the endothermic peak in the temperature interval of 800-850°C in the differential-thermal analysis curve technogenic residues formed during mechanical processing of Sastobe carbonate rocks showed that it mainly consists of calcium carbonate. Studies have shown that fine and coarse aggregates based on carbonate rocks have a rough surface, which increases their specific surface area and ensures a strong bond with the cement stone. At the same time, technogenic waste contains 2-3% powder fraction up to 0.16 mm, this fraction serves as an active mineral mixture. As a result of research, the use of these wastes as fillers can reduce the consumption of traditional crushed stone and sand by 50% without reducing the physical and mechanical properties of concrete, replacing 50% of traditional fillers with technogenic fillers based on carbonate rocks, increasing the density of concrete (2490kg/m^3), reducing its water absorption (0.66 %), strength (49.8 MPa) and frost resistance (F400) indicators made it possible to obtain concrete that is the same as the control sample and to reduce its cost without reducing the physical and mechanical properties of concrete and to improve the environmental conditions of the region.
Keywords: waste, carbonate rocks, concrete, fillers, physical and mechanical properties of concrete.

1. Introduction

In our country, the scope of involving of waste generated during the enrichment and processing of minerals is very low, only 20% is used as secondary raw materials, of which about 10% is used for building materials. The ability of the natural environment shows that it cannot process all the wastes of human activities, and the accumulated waste stock threatens the global pollution of the environment and the deterioration of natural ecosystems. Land restoration and return to economic use lag far behind the pace of their alienation. Therefore, the “Green economy” has become one of the most urgent issues in the world, including Kazakhstan. One of the main directions of the “Green economy” is the “Introduction of the waste management system” [1], [2].

Technogenic waste is solid, liquid, and gaseous production waste that is formed at enterprises in the process of obtaining the final product from raw materials.

Currently, there are two main approaches to decontamination of production waste, the first is to clean production facilities from harmful waste, and the second approach is the integrated use of natural resources, the development and implementation of effective production technologies that produce no or little waste. And one of the main sectors of the economy that allows efficient use of production waste is the construction industry, for example, 30 million tons of various wastes are effectively used annually in cement production alone [3].

Currently, there are more than 30 billion tons of waste in the Kazakh steppe. 6.7 billion of it is toxic, and 5 billion is mining debris. According to statistics, today only 10% of waste collected in the country is recycled, and 90% remains in the same state [4]. The construction industry has the potential to reuse 25-27% of the total volume of waste, but currently uses only about 4% of this raw material [5].

Research shows that only the southern regions of Kazakhstan, have a huge stock of waste suitable for the production of construction materials accumulated, the main stock of man-made waste is rocks, in particular, the heaps of the Lenger coal plant (more than 1 million tons), the polymetallic waste of the Ashchysai plant (182 million tons), carbonate wastes of the holding “Construction materials” (5.4 million tons), metallurgical wastes of JSC “Yuzhpolimetal” lead production (2.3 million tons), etc. [6].

Therefore, the use of mining waste in the production of construction materials and products is an urgent issue that not only reduces the cost of construction materials but also prevents environmental pollution.

An inexhaustible source of the raw material base of construction materials is the waste of the mining industry complex, including carbonate rocks. During the mechanical processing of rocks, unconditioned stone fragments of different fractions and shapes and waste in the form of highly dispersed powder are formed.

Studies show that the harmful effects of this waste spread to a region of 1.2 km, of which the accumulation of carbonate dust in the region between 150-650m is more than normal, and at the same time the pollution of the Earth's crust is at a very high level, and the main polluting components are chromium, lead, cobalt, zinc and iron [7].

Therefore, the integrated use of residues formed during the production of carbonate rocks not only reduces the cost of the resulting product but also increases the energy efficiency of production and improves the environmental situation in the region. Portland cement production is the largest use of technogenic waste from carbonate rocks. In the cement industry [8], in particular, the Mukhtar Auezov South Kazakhstan University is conducting research work on the production and study of composite slag-alkaline binders with local mineral mixtures and concrete based on them [9]. In [10] authors show that the production of mixed binders obtained by replacing a part of Portland cement clinker with highly dispersed active additives allows reducing carbon dioxide emissions to the atmosphere by 307 kg, to improve technical and economic indicators of Portland cement production.

In [11], [12] authors use limestone and its waste from mechanical processing in cement production, and as a result of studying the hydration patterns of cement based on carbonate additives, offer optimal compositions of concrete with the necessary operational properties.

However, there is a lack of research on the use of technogenic waste during rock processing of carbonate rocks in heavy concrete technology and on the study of adhesion processes in the contact zone between cement stone and calcium carbonate. Therefore, the development of the technology for decontamination of technogenic wastes generated during the mechanical processing of carbonate rocks by obtaining concretes with the necessary operational properties is an urgent issue.

The purpose of the work is to study the possibility of using technogenic waste formed during the mechanical processing of Sastobe carbonate rocks as a filler in heavy concrete and optimize the composition of heavy concrete.

2. Methods

We studied the possibility of using technogenic waste generated during the mechanical processing of Sastobe carbonate rocks in the production of construction materials and the physical-mechanical and chemical-mineralogical characteristics of selected technogenic waste.

X-ray diffractometric analyses were carried out using a Bruker D&ENDEAVOR instrument using a β filter with Cu-irradiation. Diffractogram recording conditions: U=35 kB; I=20 mA; capture Q-2Q; detector 2grd/min. Diffractogram analysis was performed using a JCDD card file, powder diffractometric database PDF2, and diffractogram data of pure minerals without impurities. The chemical composition of the waste (SEM) was determined by the method of raster electron microscopy carried out on a JEOL-6490 LV electron microscope. All analyses were carried out in the accredited laboratory of Mukhtar Auezov South Kazakhstan University – Regional Engineering Testing Laboratory "Structural and Biochemical Materials".

3. Results and Discussion

The results of the physicochemical analysis of technogenic residues formed during mechanical processing of Sastobe carbonate rocks are shown in Figures 1 and 2, and Table 1 below.

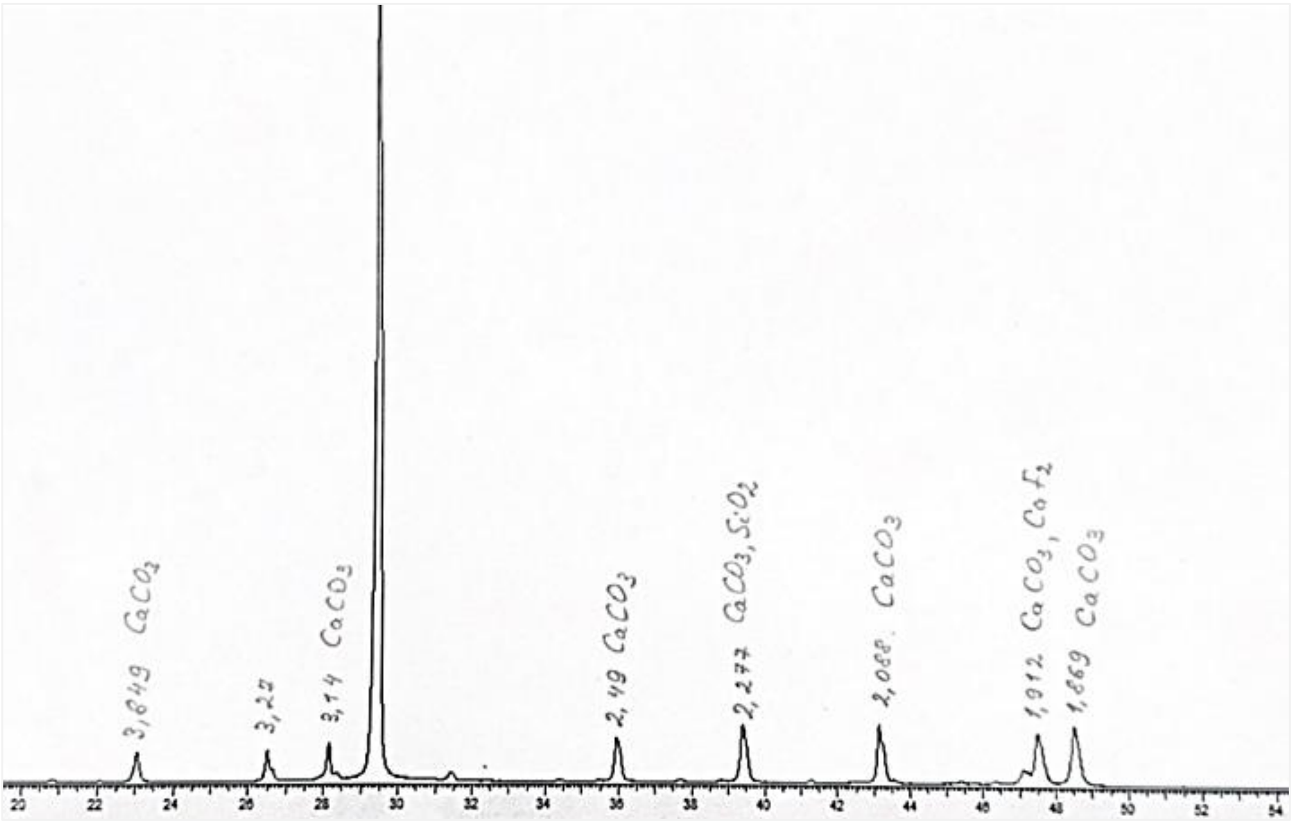
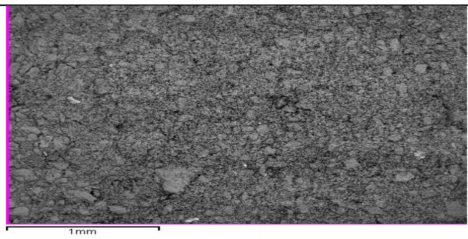


Figure 1 – X-ray diffractometric analysis results of technogenic waste

Table 1 – Results of analysis of technogenic waste by the method of raster electron microscopy

Element	Weight, %	Oxide	Weight, %
C	13.97	-	-
O	46.79	-	-
Na	0.45	Na_2O	0.61
Mg	0.33	MgO	0.55
Al	0.40	Al_2O_3	0.76
Si	1.21	SiO_2	2.59
S	0.44	-	-
K	0.18	K_2O	0.22
Ca	35.77	CaO	50.04
Fe	0.45	Fe_2O_3	0.64
Total	100.00		



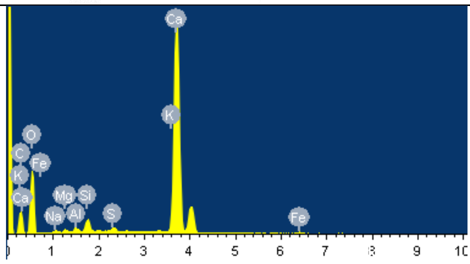
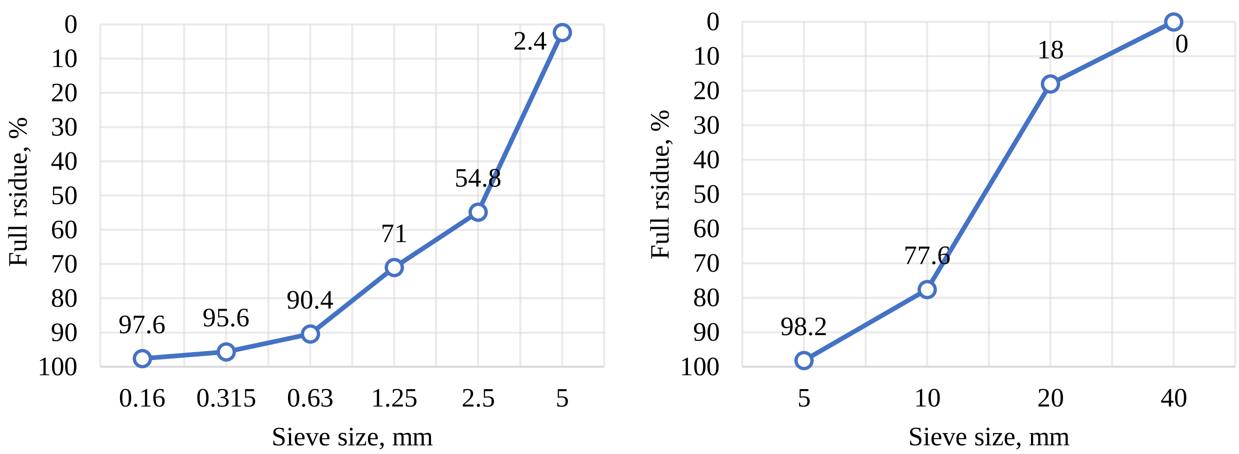


Figure 2 – Results of raster differential thermal analysis of technogenic residues formed during grinding of Sastobe carbonate rocks

The results of the physicochemical analysis show that technogenic waste formed during the mechanical processing of Sastobe carbonate rocks mainly consists of calcium carbonate $CaCO_3$ d=(3.849-3.14-2.49-2.277-2.088-1.912-1.869 A^0). The endothermic peak in the DTA curve in the temperature interval of 800-850°C is explained by the decomposition of the original calcium carbonate into calcium oxide with the release of carbon dioxide [13], [14]. X-ray diffractometric analysis also showed a small amount of quartzite SiO_2 d=(2.77 A^0), fluorite CaF_2 d=(1.912 A^0) minerals, and the analysis of the chemical composition of the mixture showed a small amount of sodium, magnesium, aluminum and iron compounds.

To achieve the goal set, the qualitative characteristics of man-made wastes were determined, and the possibilities of using technogenic wastes formed during the grinding of Sastobe carbonate rocks as a filler and mineral admixture in the production of heavy concrete were studied. Physical and mechanical properties of crushed stone and sand based on man-made waste were studied following the requirements of GOST 8735-88 ST RK 1217-2003 (Figure 3, Tables 2 and 3).



a) Granular composition of Sastobe carbonate waste (sand) μm=4,1

b) Granular composition of Sastobe carbonate waste (crushed stone)

Figure 3 – Granular composition of technogenic waste

Table 2 – Main characteristics of sand based on technogenic wastes formed during grinding of Sastobe carbonate rocks

Magnitude modulus	Intergranular cavity, %	True density, kg/m^3	Bulk density, kg/m^3
4.1	42.5	2220	1276

Table 3 – Characteristics of crushed stone based on technogenic wastes formed during crushing of Sastobe carbonate rocks

Cavity	True density, kg/m^3	Bulk density, kg/m^3	Grinding mark
42.5	2500	3300	M800

Studies have shown that fine and coarse aggregates based on carbonate rocks have a rough surface, which increases their specific surface area and ensures a strong bond with the cement stone. At the same time, it can be seen from the data of Figure 3 that technogenic waste contains 2-3% powder fraction up to 0.16 mm, this fraction serves as an active mineral mixture.

The use of such a fine fraction in concrete destroys all weak bonds with cement stone and leads to the formation of very strong, energetically strong homogeneous micro-particles. The smaller the size of the particles of the fine fraction during waste grinding, the more thermodynamically active they become. Micropowders are integrated into the concrete structure and increase the specific surface of cement particles [15].

Tables 4 and 5 show the qualitative indicators of fine and coarse aggregates based on technogenic waste generated during the grinding of Sastobe carbonate rocks.

Table 4 – Qualitative indicators of crushed stone based on technogenic waste formed during grinding of Sastobe carbonate rocks

Total residue on the sieve (%), mm				Intergranular cavity, %	True density, kg/m^3	Bulk density, kg/m^3	Grinding mark
5	10	20	40				
95.6	56.6	10.8	-	47.5	2500	1312	D600
90-100	30-60	≤10	≤0.5	≤48	2500	1800	≥D400

Table 5 – Qualitative indicators of sand based on technogenic waste generated during crushing of Sastobe carbonate rocks

Total residue on the sieve (%), mm						Magnitude modulus	Intergranular cavity, %	True density, kg/m^3	Bulk density, kg/m^3
5	2.5	1.25	0.63	0.315	0.16				
2.4	54.8	71.0	90.4	95.6	97.6	4.1	42.5	2220	1276
15			65-75			3.5			

Studies have shown that aggregates based on technogenic waste generated during the crushing of carbonate rocks meet the requirements of the state standard. «Another advantage of carbonate rocks is their cheapness compared to other components of concrete, both large-grained fractions and finely dispersed particles of these wastes can be used as local raw materials for the production of concrete with improved properties, it is characterized by good workability and low density compared to other known concrete components. Depending on the properties of the carbonate composite, limestone can act in two ways: as an inert material, replacing dense and, accordingly, heavy structural elements from other minerals, and as a fine mineral filler, it can act chemically concerning cement stone [13].

For further studies, the composition of heavy concrete was selected by replacing a certain part of natural aggregates with waste-based aggregates.

Tables 6 and 7 show concrete compositions replaced by 25%, 50%, and 100% man-made waste of traditional fillers and the main physical and mechanical properties of concrete mix and concrete.

Table 6 – Composition of concrete with fillers based on technogenic waste formed during grinding of Sastobe carbonate rocks

Composition of concrete	Cement	Crushed stone	Sand	Water
Concretes based on traditional aggregates	432	1200	720	182
Composition of Sastobe carbonate waste 25%	432	300	180	182
Composition of Sastobe carbonate waste 50%	432	600	360	182
Composition of Sastobe carbonate waste 100%	432	1200	720	182

Table 7 – Effect of technogenic aggregates on the main characteristics of the concrete mixture

Concrete mix composition	Movability(cm)
Concretes based on traditional aggregates	8
Composition of Sastobe carbonate waste 25%	6
Composition of Sastobe carbonate waste 50%	5
Composition of Sastobe carbonate waste 100%	3

The study of the effect of fine and coarse aggregates based on carbonate waste on the main characteristics of the concrete mixture showed that the water demand of the mixture gradually increases as the proportion of technogenic waste increases. If the W/C ratio is the same, as the proportion of waste increases, the rigidity of the concrete mixture increases, which is explained by the high specific surface area and porosity of non-conditioned aggregates.

It was found that the technogenic waste has no significant effect on the concrete density, as shown in Figure 4, the complete replacement of aggregates with waste from the mechanical processing of carbonate rocks increases the density of concrete by 2% compared to the control composition. This is mainly because the fine fraction in the carbonate waste increases the volume of the cement paste and fills the pores and interspaces of the filler.

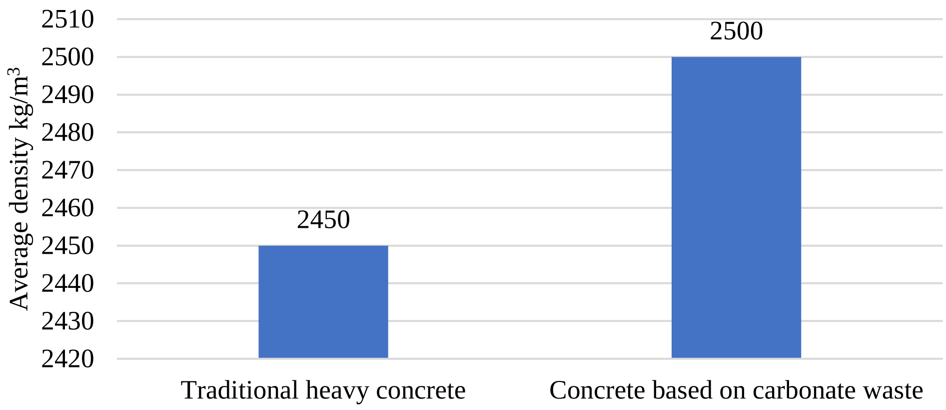


Figure 4 – Density of concrete with aggregates based on technogenic wastes formed during grinding of Sastobe carbonate rocks

Table 8 and Figure 5 show the effect of technogenic aggregates on the strength gain kinetics of concrete

Table 8 – Effect of technogenic aggregates on the kinetics of strength gain of concrete

Concrete composition	Strength 7 days, MPa	Strength 14 days, MPa	Strength 28 days, MPa
0	33.7	51.4	51.7
1	32.7	34.1	32.1
2	33.6	45.8	49.8
3	29.6	37.0	49.5

Compared to the control sample, the strength gain kinetics of the samples based on man-made aggregates is somewhat lower, however, the strength gain kinetics and the tensile strength of the samples replaced with 50% man-made waste were found to be close to the control sample.

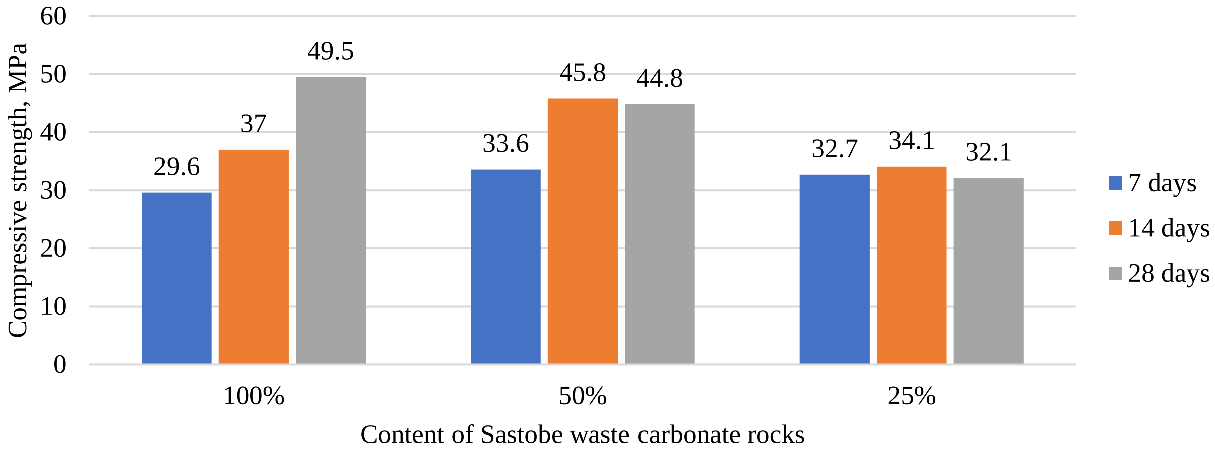


Figure 5 – Effect of technogenic aggregates on the strength gain kinetics of concrete

Authors of the works [16] show that “hardening cement paste based on Portland cement forms calcium carbonate of different composition in $CaCO_3$-$Ca(OH)_2$-H_2O system when reacting with carbonate filler. It is noted that calcium carbonate crystals are relatively small in size and can be freely located among hydration products, different from $Ca(OH)_2$ crystals.

According to Table 4, used technogenic waste contains 2-3% highly dispersed (0.16 sieved) waste. Based on the data of this work [17], it affects the chemical activity of carbonate rocks, and in the “carbonate-cement” system, calcium hydrocarboaluminate $3CaO\cdot Al_20_3\cdot CaC0_3\cdot 11H_20$, hydrocarbonate – $CaC0_3$-$Ca(OH)_2\cdot H_20$, and hydrosulfocarbosilicate (thaumasite) $CaO\cdot SiO_2\cdot CaS0_4\cdot CaC0_3\cdot 15H_20$ is formed.

Figure 6 shows an electronic image of the contact area between cement stone and carbonate aggregate.

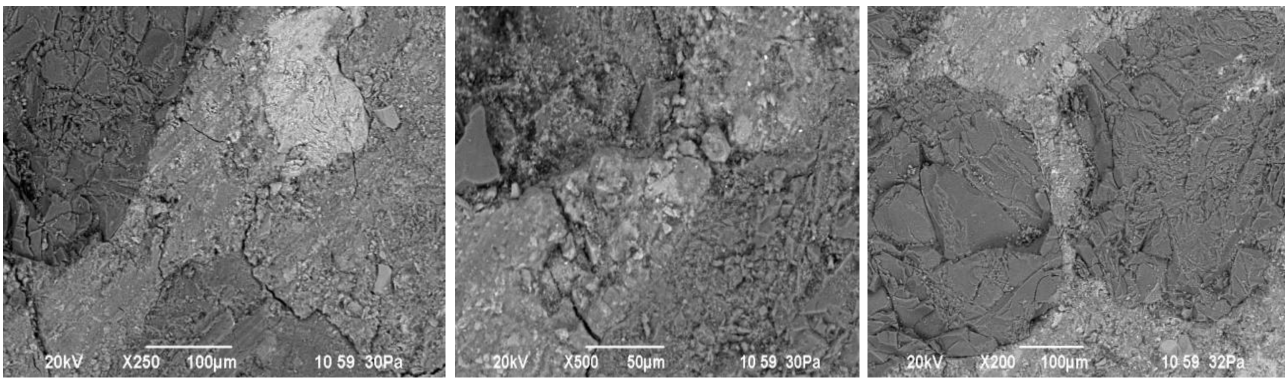


Figure 6 – Electron image of the cement stone and carbonate aggregate contact zone

As can be seen from Figure 8, due to the roughness of the surface of the fillers, close contact adhesion is observed, as well as traces of calcium carbonate formed as a result of the carbonization of calcium hydroxide.

In general, the adhesion strength of the aggregate to the cement stone is a determining factor of the overall strength of the concrete. According to the data of the work [18], the adhesion strength of cement stone with filler grains depends on several factors, namely, the shape, roughness, and cleanliness of the filler grains, the chemical and mineralogical composition of the filler grains, the strength of the cement stone, the presence of mineral additives that increase the adhesion strength, micro defects of the structure in the contact area.

Table 9 shows the physical and mechanical properties of concrete based on technogenic aggregates formed during the grinding of Sastobe carbonate rocks.

Table 9 – Physical and mechanical properties of concrete based on technogenic aggregates

Concrete composition	Density kg/m^3	Water absorption, W%	Frost resistance (F), cycles
0	2450	0.67	F400
1	2500	0.98	F300
2	2490	0.66	F400
3	2550	0.73	F200

The frost resistance of the samples was determined by the accelerated method, the frost resistance of the concrete can be increased by reducing the W/C ratio and increasing the proportion of closed pores in the concrete body by adding air-entraining admixtures. In our case, as a result of an increase in the concrete density due to the deep penetration of the cement paste into the filler grains, the water absorption of the concrete decreases, and the frost resistance of the sample increases.

4. Conclusion

1. Technogenic waste formed during mechanical processing of Sastobe carbonate rocks mainly consists of calcium carbonate $CaCO_3$ d= (3,849-3,14-2,49-2,277-2,088-1,912-1,869 A^0), in addition, of a small amount of quartzite SiO_2 d=(2, 77 A^0), fluorite CaF_2 d=1.912 A^0 minerals, a small amount of sodium, magnesium, aluminum and iron compounds.

2. It was found that the use of technogenic waste formed during the mechanical processing of carbonate rocks as a filler allows to reduce the consumption of traditional crushed stone and sand by 50% without reducing the physical and mechanical properties of concrete.

3. Studies have shown that the replacement of 50% of traditional aggregates with technogenic aggregates based on carbonate rocks increased the density of concrete to 2490 kg/m^3, decreased its water absorption to 0.66%, increased its compressive strength to 49.8 MPa, and frost resistance to F400, which was the same as the control sample.

4. The use of technogenic aggregates formed during the mechanical processing of carbonate rocks in heavy concrete technology allows for a reduction in the cost of concrete. It improves the environmental condition of the region without reducing the physical and mechanical properties of concrete.

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Ruslan Kudabayev – drafting, testing.

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