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Research Article

Recycling of Gangue Mineral (Pasa) and Its Use in Filled Concrete

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Abstract:

Aggregate is one of the most important raw materials used in areas such as concrete production, asphalt industry and filling raw material. Most of the aggregates are produced in aggregate quarries, sand and gravel beds. The remaining aggregates consist of recycling of industrial wastes (10%), slag and ashes and debris (8%), marine and industrially produced aggregates (4%). The aggregate industry plays a key role in the functioning of the construction industry's supply chain. However, the fact that natural aggregates are being depleted day by day has led to other aggregate types. Eti Krom Inc. is the world's largest marketable hard lump chrome ore producer. Gangue minerals (pasa) are the rocks that are obtained by the extraction of chrome ore and contain worthless minerals. While some of the gangue minerals are returned to the mine, a large part of it creates a problem as worthless waste. In this study, it is aimed to use the gangue minerals, which is produced in mining activities in Eti Krom Plant, as an aggregate, in the filled concrete. Samples were prepared under laboratory and process conditions. The mechanical properties of the samples were analysed by water absorption, porosity, methylene blue and compressive strength tests. In addition, the characterization analyses of the samples were made with XRD, XRF and SEM/EDX analyses. As a result, it has been observed that the use of gangue minerals as aggregate in the filled concrete can be used as an alternative to natural aggregate.

1. Introduction

Concrete; it is obtained by mixing aggregate, cement, water and, when necessary, additives used to give some extra properties to concrete in the most appropriate proportions. Concrete is a homogeneous, isotropic and composite building material that initially has plastic properties and can be easily processed, and gains strength by setting as a result of the hydration of the cement in its composition with water after being placed in the mould. Concrete consists of 75% aggregate, 10% cement and 15% water by absolute volume. When necessary, additives can be added, provided that they are not more than 2% of the cement weight [1]. The mixture aggregates used in concrete production are one coarse grained and the other fine grained. Concretes are obtained by mixing at least two aggregates with different grain distributions in proportions in accordance with standards [2].

The only reason for using aggregate in concrete production is not to produce more economical concrete. Aggregates are very important because they form the carrier skeleton of concrete. Aggregate also contributes significantly to the technical properties of concrete [3]. The durability, porosity, water permeability, mineral structure, grain shape, gradation, surface roughness of the grains, largest grain size, modulus of elasticity, and elasticity of the aggregate used in concrete affect the concrete properties [3, 4].

Filling in mining; It is the process of filling an area opened by production, partially or completely, using hand, gravity, mechanical, pneumatic and hydraulic tools. The concrete used for this purpose is called filler concrete. The development of filling technology in the world and efforts to benefit from it have made great progress in the last twenty years. The mining industry is particularly interested in this technology for filling large productive open spaces underground [5].

The gangue mineral occurs during the extraction of chromite ore. Pasa; It is defined as material that does not contain mineralization or cannot be enriched according to current economic and technical conditions, but has to be produced as a result of the operation and has not been subjected to any process other than excavation. Ferrochrome production facilities and marble quarries are among the mining branches where a lot of pasa is produced. It may require quite large areas to store this size of material. These areas are regularly monitored with analysis and activity reports in line with the relevant legislation, and in case the operating license expires, the transportation of pasa materials is required within six months at the latest, in accordance with the relevant legislation [6, 7].

Aggregate (sand, gravel, crushed stone), which has the largest proportion (about 75%) among the materials that make up concrete, is increasing its strategic importance in the ready-mixed concrete sector day by day, as a material whose natural resources are gradually depleted and clean, high-quality samples that comply with standards are difficult to find [3, 6]. Therefore, it is very important to create alternative aggregate culture. One of the alternatives to be suggested is the use of pasa material as aggregate.

Eti Chrome Inc. is the world's largest high carbon ferrochrome (HC FeCr) producer. Pasa material are occurred in mining activities where chrome ore is obtained. In this study, pasa material was used as aggregate in filler concrete. The mechanical properties of the prepared filled concrete samples were analysed by water absorption, porosity, methylene blue and compressive strength tests. In addition, characterization analyses of the samples were carried out using XRD, XRF, SEM/EDX analyses. As a result, it has been observed that the use of gangue mineral as aggregate in filled concrete can be used as an alternative to natural aggregate.

2. Material and Methods

In this study, the usability of pasa material from the mine as aggregate in filled concrete was investigated. Pasa materials were supplied from Eti Chrome Inc.'s KEF/Elazığ mine site. Crushing processes of the pasa material into 0-4 mm and 4-50 mm were carried out. Then, porosity and water absorption tests of the aggregates were performed. The results obtained are given in Table 1. TS EN 1097-6, AASHTO T84, ASTMC 128 standards were used in fine aggregate water absorption and porosity tests. TS EN 1097-6, AASHTO T85, ASTMC 128 standards were used in coarse aggregate water absorption and porosity tests. In addition, sieve analyses of the aggregates were performed and gradation and granulometry curves were created. The resulting graphics are given in Figure 1.

Table 1. *water absorption and porosity tests*

Coarse Aggregate Water Absorption and Porosity Tests (4-50 mm)			
Water Absorption	% 1,52	Porosity	% 4,34
Fine Aggregate Water Absorption and Porosity Tests (0-4 mm)			
Water Absorption	% 4,69	Porosity	% 11,44

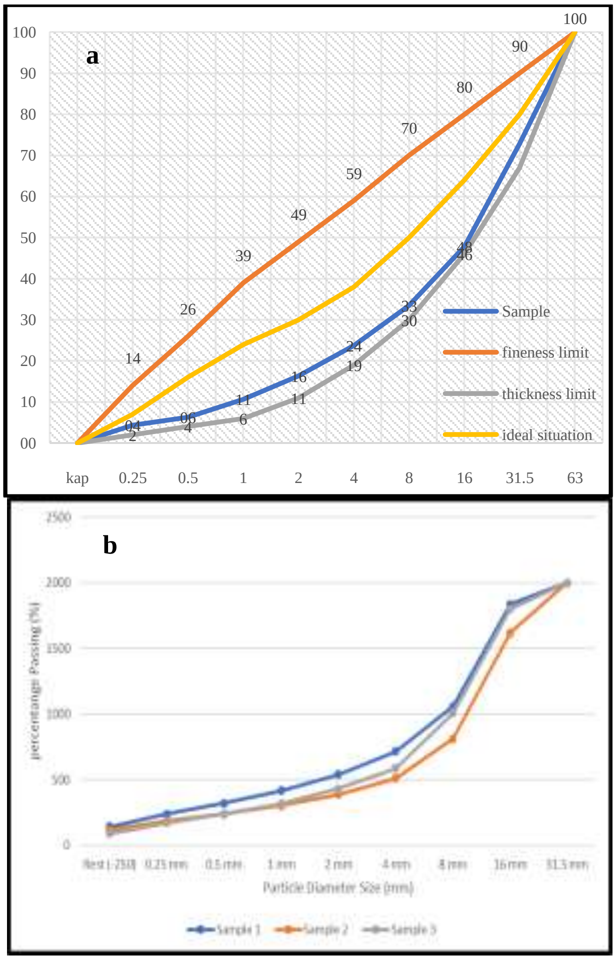

Figure 1. *Pasa material gradation and granulometry curves (a; gradation curve for pasa material, b; granulometry curve for pasa material)*

Alkali-silica reactivity (ASR) test of the waste material was carried out according to ASTM C1260 standards. In addition, methylene blue tests of the pasa material were carried out according to TS EN 933-9 standard. Concrete samples were prepared according to the recipe given in Table 2 (for 15 samples). The prepared samples are given in Figure

2. The prepared concrete samples were kept in the curing pool for 7, 14 and 28 days. 5 samples were taken as reference for each waiting period. Uniaxial compressive strength tests were performed. XRF (X-ray Fluorescenc) analysis of the pasa material used were performed. After the compression test, characterization studies of the samples were carried out using SEM (Scanning electron microscopy) and XRD (X-Ray diffraction) analyses.

Table 2. *Filled concrete recipe used in experimental studies (for 15 samples)*

Materials	Weight (kg)
Concrete	6.2
Gangue (pasa, 0-4 mm)	30.6
Gangue (pasa, 4-50 mm)	37.4
Water (L)	5 (L)

Figure 2. *Prepared samples*

3. Results and Discussions

XRF analyses of the pasa material used in experimental studies are given in Table 3.
The chemical content of the aggregate used in filled concrete is important. Because the SiO_2+Al_2O_3+Fe_2O_3 ratios and MgO/CaO ratios contained in the aggregate are effective in increasing properties such as mechanical strength and alkaline activity. For example, high MgO content increases resistance to alkaline activity. However, increasing the percentage of MgO mineral in the rock does not increase the compressive strength of limestone and dolomites [8, 9].

Table 3. *XRF analyses of the pasa material*

Pasa (0-4 mm)	**Mg**	**Al**	**Si**	**S**	**Cl**	**K**	**Ca**
	40.36	0.64	38.06	0.02	0.02	0.02	0.83
	Cr	**Mn**	**Fe**	**Co**	**Ni**	**Zn**	**Ba**
	1.08	0.27	17.68	0.04	0.86	0.01	0.1
Pasa (4-50 mm)	**Mg**	**Al**	**Si**	**S**	**Cl**	**K**	**Ca**
	40.26	0.59	38.49	0.02	0.02	0.01	0.83
	Cr	**Mn**	**Fe**	**Co**	**Ni**	**Zn**	**Ba**
	0.91	0.27	17.58	0.04	0.86	0.01	0.1

Alkali-silica reactivity (ASR) test results are given in Table 4. Alkaline silica reactivity (ASR) tests were carried out using “CEM II 42.5 bulk cement” according to ASTM C1260 standards. The average expansion value of the test samples given in Table 4 when kept in 80 °C and 1M NaOH solution for 14 days is given. Thermal expansion of the samples arising from the temperature difference between 20 °C and 80 °C was deducted. Since the expansion value obtained in 14 days for the fine aggregate and CEM II 42.5 bulk cement used in the experiment and the mortar bars produced in accordance with the standard is lower than the 0.10% limit values recommended for the ASTM C1260 test method, the fine aggregate-cement mixture used in these experiments It was observed that there was no potential expansion problem for the current experimental conditions.

Table 4. *Alkali-Silica Reactivity (ASR) test results*

Aggregate-Code	14-days average expansion, %	ASR
Sample 1	0.007	Not
Sample 2	0.008	Not
Sample 3	0.003	Not

The standards generally used in methylene blue tests are TS EN 933-9, AASHTO T 330, ASTM C 837-09. The main purpose of this test is to determine the amount of clay and silt in the aggregate mixture. Because the excess of undesirable structures such as clay and silt in the aggregate causes a decreasing effect on the strength of concrete. Clay and silt are materials that absorb methylene blue. If the amount of clay and silt in the mixture is higher, the amount of methylene blue (MB: Methylene Blue) used will be higher. Methylene blue tests were carried out on the waste material. TS EN 933-9 standard was used in this experiment. The results of methylene blue are given in Figure 3. These results showed that it is possible to use pasha as aggregate because there are almost no undesirable structures such as clay and silt.

Figure 3. *Results of methylene blue*

Concrete samples were kept in curing water for 7, 14 and 28 days. Uniaxial compressive strengths of a total of 15 specimens, 5 specimens for each group (7, 14 and 28 days) were tested. compressive strength test results are given in Figure 4.

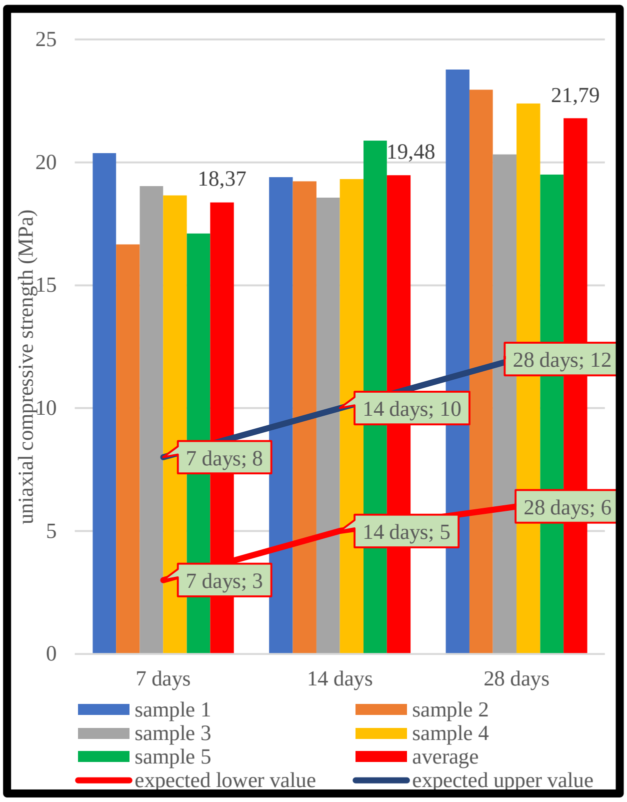

Figure 4. *uniaxial compressive strength test results*

The minimum and maximum expected compressive strength values according to the waiting time in curing water are available. These values are 3-8 MPa, 5-10 MPa and 6-12 MPa for concrete specimens kept in curing water for 7, 14 and 28 days, respectively. Uniaxial compressive strength results are also the most important parameter in filled concrete. Because this result gives the most definite information about whether or not the infill concrete can be used in mines. The use of gangue (pasa) as aggregate in filled concrete increased the uniaxial compressive strength. It is also seen in Figure 4 that as the waiting time in curing water increases, the compressive strength increases more. This result shows that the gangue (pasa) mineral can be used as an alternative aggregate to limestone aggregate in filled concrete.

Industrial wastes with suitable chemical, pozzolanic and mineralogical properties are stored on agricultural soils, causing environmental damage [10]. The gangue mineral consists of minerals that do not contain enrichment and its storage in stockpiles causes environmental problems. This study has shown that approximately 200.000 tonnes of limestone aggregate can be used as a substitute for the gangue mineral annually. The use of 200.000 tonnes of pasa instead of limestone aggregate is extremely important in terms of saving approximately 77% of the cost.

SEM analyses of concrete samples kept in curing water for 7, 14 and 28 days are given in Figure 5. During cement hydration, each main component reacts with water and different hydration compounds are formed by each main component at the end of hydration [10, 11]. While pozzolanic materials reduce the amount of slaked lime by reacting with $Ca(OH)_2$ formed as a result of hydration, they increase the resistance against aggressive environmental factors, and additional C-S-H gels formed as a result of the reaction strengthen the gel structure. Increased gel strength improves the microstructure of the concrete and increases the compressive strength and tensile strength as a more dense and impermeable structure is formed [12, 13]. When the results of the studies in which nano materials are included are analysed, nano materials fill the pores, consume calcium hydroxide ($Ca(OH)_2$), which is an undesirable material in concrete, improve the interface transition zone by increasing C-S-H gel formation, contribute to the formation of a denser matrix, and increase the compressive and flexural strength, fracture toughness, tensile strength and resistance to cracking of concrete.Figure 4 shows that a dense, homogeneous and stable C-S-H phase is formed. The results obtained from SEM images support the uniaxial compressive strength results. XRD analyses of concrete samples kept in curing water for 7, 14 and 28 days are given in Figure 6. The region shown with a ring in Figure 6 is the common phases in cement hydrolysis (such as CH, C_2S, C_3S

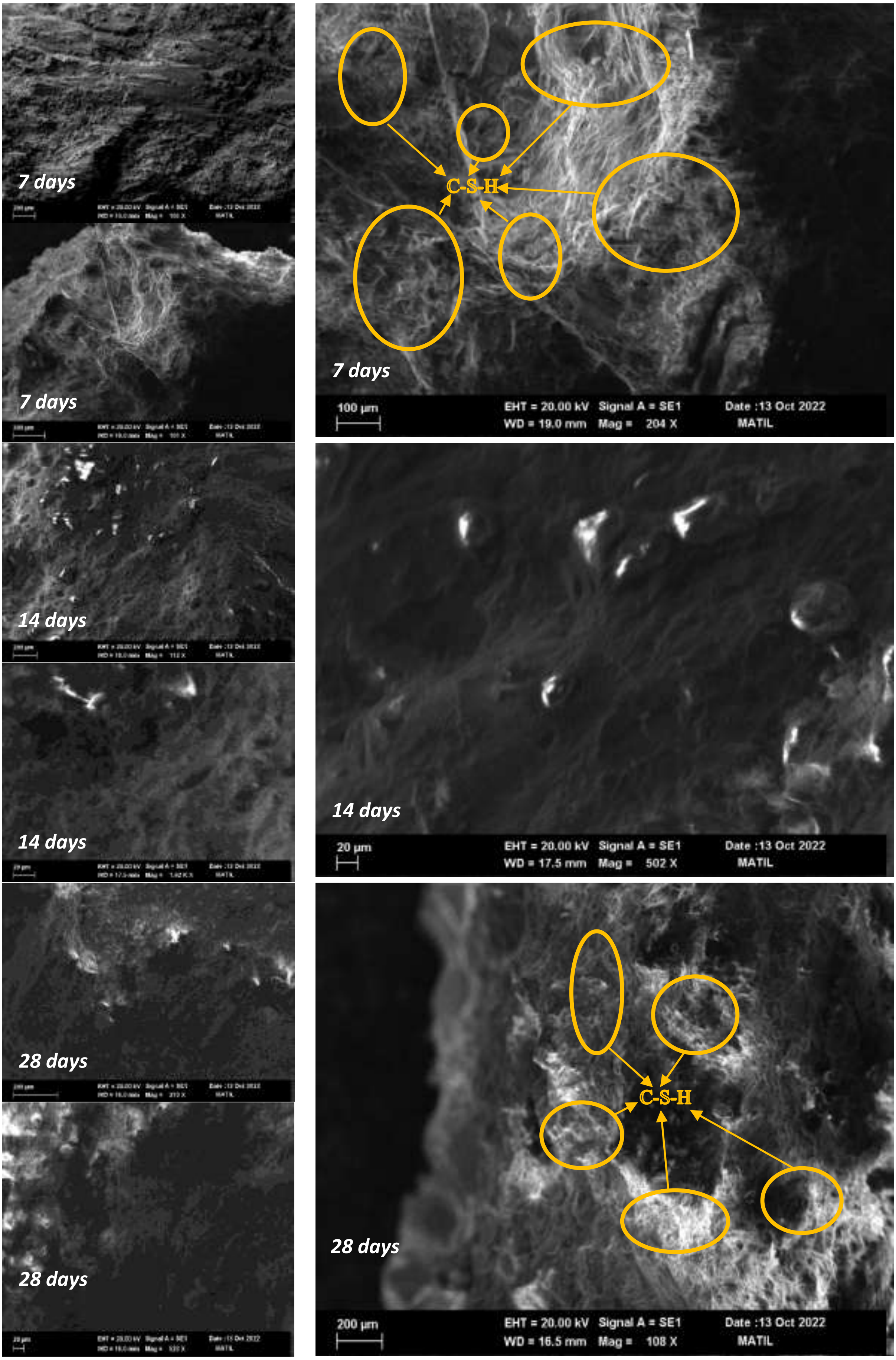

Figure 5. *SEM analyses of concrete samples, a) 7 days, b) 14 days, c) 28 days*

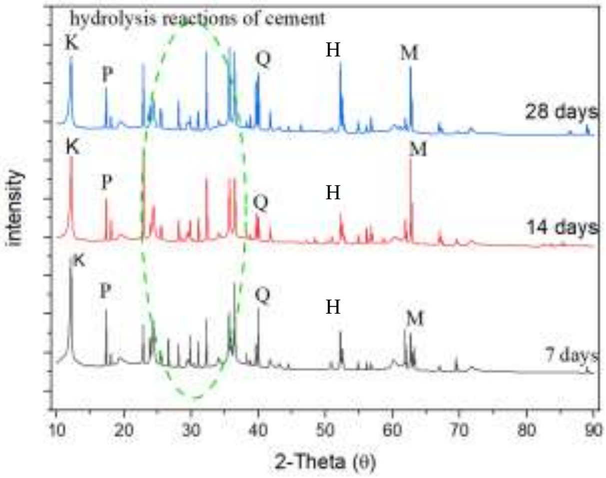

Figure 6. *XRD analyses of concrete samples, a) 7 days, b) 14 days, c) 28 days (K: Kaolinite ($Al_2Si_2O_5(OH)_4$), P: Portlandite ($Ca(OH)_2$, Q: Quartz (SiO_2), H: Hematite (Fe_2O_3), M; Magnesium Oxide (MgO))*

and $CaCO_3$) [14-17]. Gangue mineral is rich in silicon, magnesium and iron (see Table 4). Therefore, phases such as kaolinite, quartz, hematite and magnesium are seen in XRD analysis. Studies [18, 19] have shown that MgO increases the strength of concrete. Therefore, the presence of hematite, magnesium oxide and silicon dioxide may have increased the uniaxial compressive strength.

Fly ash reacts with $Ca(OH)_2$, one of the hydration products of Portland cement, and shows pozzolanic properties. Calcium-silicate-hydrate (C-S-H) and calcium aluminate silicate hydrate products (C-A-S-H) are formed from this pozzolanic reaction. XRD analysis shows the formation of Ca $(OH)_2$ phases. It is also seen that the peaks of this phase decrease with the increase in curing time (7, 14 and 28 days). The decrease in $Ca(OH)_2$ peak intensities can be explained by the increase in the C-S-H phase. This result supports the SEM analysis. In addition, the decrease in $Ca(OH)_2$ peak intensity increases the compressive strength of cement and concrete [11, 20]. This result supports the uniaxial compressive strength results.

There are very few studies on the use of gangue mineral (pasa) as an alternative to limestone aggregate in fill concrete. The studies have shown that the gangue mineral (pasa) can be used as aggregate in the fill concrete. The results have shown that the use of pasa material as an alternative to limestone aggregate not only reduces the cost but also shows that resources can be used more beneficially within the scope of zero waste.

4. Conclusions

In this study, the use of gangue mineral (pasa) as aggregate in filled concrete was investigated.

- Considering the strength values expected from filled concrete, it is appropriate to use pasa as aggregate.
- Experimental studies have shown that the sufficient strength expected from filled concrete is provided.
- Alkali-silica reactivity test (ASR) of the pasa material was carried out and it was observed that there was no potential expansion problem under the current test conditions.
- The experimental study confirmed that it is possible and successful to use pasa material as aggregate in filled concrete. Analyses (SEM, XRD etc.) have supported this phenomenon.
- It has been determined that when we use pasa material instead of limestone aggregate in filled concrete***, the cost will be reduced by 77.06%.***

Author Statements:

- **Ethical approval:** The conducted research is not related to either human or animal use.
- **Conflict of interest:** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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- **Author contributions:** The authors declare that they have equal right on this paper.

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- **Data availability statement:** The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

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