EXAMINATION OF UTILIZATION OF GYÖNGYÖSOROSZI FLOTATION TAILING MATERIAL AS AGGREGATE FOR CONCRETE

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Abstract
Utilization of mining wastes as secondary raw materials is of great importance. Utilization of ore processing wastes, often presented in a great volume, containing pyrite and other heavy metal sulphides in environmentally hazardous concentrations, could mitigate the environmental problems by decreasing the stored volume of the waste, hereby decreasing the dissolved heavy metal content. Such utilization can be the application of tailings as concrete aggregate.

Considering the fact, that the oxidation process of sulphides could continue in the solidified concrete, the study of its influence on the components of the concrete is crucial. The intermediate and by-products of the bacterially catalyzed electrochemical oxidation of the pyrite are secondary minerals (e.g. ferri-oxides, ferri-oxihydroxides and gypsum). The pyrite-rich grain in consequence of the electrochemical alterations will enlarge its volume, by doing so internal stresses will be generated in the concrete. The oxidation process generates acidic fluids which begin to dissolve the other components of the concrete (Ca-hydroxides, C-S-H-gel). Close to the surface of the solidified concrete body the products of the oxidation will cause the appearance of conspicuous tail-like brown patches. The above mentioned phenomena cause the strength decreasing of the concrete and confinement of the application on fully visible surfaces.

The aim of the present study, using mineralogical methods, is establishing whether the approximate 2.5 million m$^3$ Gyöngyösoroszi flotation tailings, deposited in the northern border of the village, is suitable for utilization as concrete aggregate.

On the material of the ZT4 shallow drill, X-ray diffraction and scanning electron microscopic measurements were carried out to investigate the mineralogical composition, with especial regard to pyrite content. Based on the examination of the oxidation process, taking place in the solidified concrete and considering the mineralogical constituents of the waste, it can be concluded that, the limitation of the possibility of applications of the solidified concrete is necessary. If the solid concrete is isolated from moisture and oxygen of the air or the bacterial catalyses of the pyrite weathering is confined, the concrete is capable of everyday usage.

1. Introduction

In this study a possible utilisation of the Gyöngyösoroszi flotation waste material as aggregate was examined.

Gyöngyösoroszi is situated in the northern-eastern part of Hungary in the Mátra Mountains. This little village is settled in the valley of Toka stream. The southern part of the valley is already the outer part of the town of Gyöngyös. All the flood area is used for agriculture. Between the main road and Gyöngyösoroszi an agricultural reservoir can be found.

The Száraz- and the Toka streams flow into this lake. Between the two valleys of these streams the flotation waste dump was established (Figure 1).
The run-of-mine ore was pre-concentrated using heavy medium separation, then by flotation process. At the end of the process, the products were Zn-concentrate (sphalerite, zinc-sulfide) and Pb-concentrate (galena, lead-sulfide), Pb-Cu by-product (galena with chalcopyrite, lead-sulfide with copper-sulfide), and pyrite (ferro-sulfide) powder. During the concentration processes in the heavy suspension phase the aqueous suspension of ferrosilicon (74–78% Fe with 10–20% silicon) was used as a heavy medium. Its remaining, very fine powder was discarded to the flotation waste dump. At the end of the 1970-s the operation of the mine became unprofitable, the mine was closed. At the end of the working period of the mine about 2.5 million m$^3$ waste was deposited. This still deposited flotation waste is an environmentally hazardous material in accordance with the new legal criteria.

The weathering of rocks and mining wastes is a natural process affecting a large variety of artificial materials and minerals. Most rock types are subjected to the transformation of some of their original components into new phases. For instance a common mineral, such as orthoclase, is progressively transformed into kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) [1]. In the natural environment these alteration processes are very slow and should be considered at the geological time scale. However the incorporation of rock as aggregate into concrete may lead to a drastic acceleration of the rock deterioration. Concrete represents quite an aggressive environment for the minerals compared to the natural conditions the rock had previously been exposed. The concrete pore liquor is mainly composed of alkaline and hydroxide ions, and the pH is generally higher than 13.0 [2].
A harmful reaction affecting rocks is the oxidation of pyrite (FeS\textsubscript{2}) and pyrrhotite (Fe\textsubscript{1–x}S\textsubscript{x}), which are common minerals, disseminated in various rock types. These minerals are unstable in the presence of water. Their oxidation leads to a series of chemical reactions and to the formation of products of a higher volume than the initial volume of materials. At first there is oxidation of the iron sulphides in the presence of water and oxygen, followed by the formation of iron hydroxide (goethite, FeOOH) and sulphuric acid:

\[
\text{FeS}_2 + 15/4 \text{O}_2 + 5/2 \text{H}_2 \text{O} \rightarrow \text{FeOOH} + 4 \text{H}_2 \text{SO}_4 \quad (1)
\]

Sulfuric acid could react with calcite (CaCO\textsubscript{3}) to form expansive gypsum (CaSO\textsubscript{4} * 2 H\textsubscript{2}O):

\[
\text{H}_2 \text{SO}_4 + \text{CaCO}_3 + 2 \text{H}_2 \text{O} \rightarrow \text{CaSO}_4 * 2 \text{H}_2 \text{O} + \text{CO}_2 \quad (2)
\]

This reaction is the source of several problems in the world, causing a large range of damage to building foundations and concrete slabs [3]. If reaction (1) occurs in an already hardened concrete, the sulphuric acid reacts with the portlandite (Ca(OH)\textsubscript{2}), which is one of the hydration products of Portland cement and gypsum is formed according to the following reaction:

\[
\text{Ca(OH)}_2 + \text{H}_2 \text{SO}_4 \rightarrow \text{CaSO}_4 * 2 \text{H}_2 \text{O}. \quad (3)
\]

The gypsum then reacts with aluminates in the cement (with its anhydrous or hydrated components as well), leading to the formation of potentially expansive ettringite (Ca\textsubscript{6}Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}(OH)\textsubscript{12} · 26H\textsubscript{2}O or in concrete chemistry (CaO)\textsubscript{3}(Al\textsubscript{2}O\textsubscript{3})(CaSO\textsubscript{4})\textsubscript{3} · 32H\textsubscript{2}O)

\[
3 \text{CaO} * \text{Al}_2 \text{O}_3 + 3 \text{CaSO}_4 * 2 \text{H}_2 \text{O} + 26 \text{H}_2 \text{O} \rightarrow (\text{CaO})_3(\text{Al}_2\text{O}_3)(\text{CaSO}_4)_3 · 32\text{H}_2\text{O} \quad (4)
\]

This secondary ettringite must be strictly differentiated from the primary ettringite normally formed in the first days of cement hydration by the gypsum and the aluminate phase of the cement (the tricalcium aluminate, 3 CaO * Al\textsubscript{2}O\textsubscript{3}). Thereafter the primary ettringite turns into a more stable form of sulfoaluminate, which is monosulfoaluminate (3CaO * Al\textsubscript{2}O\textsubscript{3} * CaSO\textsubscript{4} * 12 H\textsubscript{2}O) and finally, into hydrogarnet (C\textsubscript{4}AH\textsubscript{13}). The remaining sulfate ions are trapped in the C-S-H gel. Secondary ettringite might be expansive; if the germination degree is higher than the crystalline growth degree the product formed will be more or less crystallized, having a molar volume three to eight times larger than that of the initial solid. If there is sufficient space for the ettringite to crystallize, needle-shaped crystals will be formed [4].

The pyrite oxidation reaction is greatly exothermic, producing about 1410 kJ of heat by a mole of oxidized pyrite, which contributes to a local increase of the temperature and accelerate the oxidation reactions of pyrite [5]. In concrete the main factor increasing the oxidation degree of pyrite, found either in frambooidal or massive form, is a high pH, related to the amount of OH-ions in the pore liquor. In concrete both forms of pyrite have the same behaviour in a high-pH solution; the higher the alkalinity of the solution, the faster the reaction is [6].

The porosity and the pore connectivity of the aggregate and concrete also represent important parameters regarding aggregate weathering, as well as concrete deterioration.
Certain aggregates are more subject to weathering and deterioration, owing to their petrographic nature. For instance schist and shale rocks have a laminar structure, which increases the permeability and porosity of the rock. Moreover shale rocks contain a certain amount of clay minerals that absorb water and oxygen. If a significant proportion of aggregate particles are cracked before their incorporation into concrete, due to tectonics or to quarrying operations, such as drilling, blasting and crushing the pyrite disseminated in the aggregate particle would then be more accessible for water and oxygen and may react faster [7].

2. Materials and methods

2.1. Field and laboratory samples

The whole area of the flotation tailing impoundment was sampled, gathering materials from the heavily oxidized upper layer of the already dried tailing pond. In the middle section of the finely ground waste heap the ZT4 drill hole is situated. Undisturbed core samples were taken from the drilled material. Each sample was at least about 200 g, and after extracting from the drilled material, the samples were closed to plastic bags to prevent undesired secondary oxidation caused by oxygen and moisture rich air.

2.2. Analytical methods

A qualitative characterization of the mining and flotation waste material as aggregate samples was performed using X-ray diffraction (XRD) analysis. XRD analysis enables the identification of the crystalline phases. Every crystalline species will give a characteristic set of diffraction peaks, whose position and intensity correspond to a specific crystalline structure. Prior to the X-ray analysis, samples were manually ground to fineness lower than 45 \( \mu \text{m} \), put and compacted on the rough surface of a glass blade to be randomly disorientated. A Bruker D8 Discovery model was used to perform the XRD analysis. The X-ray beam was produced by a tube, that consists of a cathode and an anode made of copper using 40 kV accelerating voltage and 40 mA heating current. The samples prepared from the cores were also observed under a scanning electron microscope (SEM). For the SEM analysis, fresh and oxidized surfaces of bulk samples were used. The originally finely ground flotation waste material was sprinkled onto a sticky surface of a plastic tape. To increase the conductivity of the surface, a thin layer of gold of 100–200 Å in thickness was applied on the face of samples. The elementary analysis of crystals detected on the surface was conducted by the energy dispersive X-ray spectrometer (EDXS). The SEM used for this study was a Jeol JXA 8600 superprobe, coupled with an X-energy analysis system. The chemical analysis using EDS was done with a Tracor EDS system (model 5500) Li/Si crystal detector and an accelerating voltage of 15 kV.

3. Results and discussion

3.1. Petrography of the aggregates

From the point of view of petrology, the material of the flotation tailing impoundment is fine-grained sand [8, 9]. If the light or dark gray quartz rich material oxidized fully or partly, the result is a yellow discoloration. The cause of the intense change in color the precipitation of jarosite and ferro-oxihydroxides mixed with gypsum. The material of the waste is more or less homogeneous. The upper heavily oxidized cover mixed with soil
contains more sulphates and ferro-oxides as well as oxy-hydroxides. The quartz content, because of the chemical stability of the so-called perfect tectosilicate structure, is constant. However the chemically stable silicon-dioxide was under stress, together with the pore fluid of the concrete it will react to form alkali silica gel structure cracking the aggregate particles and the concrete. The pyrite content is about 5%. This mineral is the main source, by its atmospheric oxidation, the further forming sulphates and ferro oxyhydroxides in the concrete. Carbonates in case they are present in any form (about 5%) might cause other problems in the concrete. The subsequent carbonation in cold wet environments can seriously crack the already solidified concrete. The generalized mineralogical composition of the fresh gray and oxidized yellow waste material using X-ray diffractometry can be seen in Table 1.

Table 1

Mineralogical composition of the Gyöngyösoroszi flotation tailing material. Mineral quantities are in mass percentages [8, 10]

<table>
<thead>
<tr>
<th>Minerals/Sample numbers</th>
<th>Gray material</th>
<th>Yellow, oxidized material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montmorillonite</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Illite</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Chlorite</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Quartz</td>
<td>61</td>
<td>54</td>
</tr>
<tr>
<td>Feldspar</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>Plagioclase</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Pyrite</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>Siderite</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>Dolomite</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Jarosite</td>
<td>3</td>
<td>7</td>
</tr>
<tr>
<td>Gypsum</td>
<td>Traces</td>
<td>4</td>
</tr>
<tr>
<td>Augite</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>x-ray amorphous</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

3.2. Sulfide minerals and secondary oxidation products under the surface of the tailing impoundment

Materials from ZT4 drill hole situated in the middle section of the tailing impoundment are illustrative of the whole tailing body. The undisturbed drill hole material was examined by optical stereomicroscope and scanning electron microscope (Figure 2).
Because of the intense crushing and grinding operations in the ore processing plant, a high amount of the tailing material is mineralogically homogenous, e.g. only pyrite- (Figure 3 and 4) and Ca-containing feldspar (Figure 5 and 6). The surfaces of these mineral grains are exceptionally well exposed to the weathering processes e.g. hydrolysis and other solvent reactions.
Figure 4: EDS spectrum of the pyrite grain

Figure 5: SEM image of a Ca containing feldspar (orthoclase)

Figure 6: EDS spectrum of the orthoclase grain
However, other parts of the tailing material consist of heavily oxidized grains. Generally the surfaces of these particles are covered with secondary minerals, mainly with sulphates (Figures 7–8, and 9.)

Figure 7: Secondary minerals (mainly lamellar gypsum crystals) on the surface of a Mn containing calcite grain

Figure 8: EDS spectrum of a gypsum crystal from the surface of the above mentioned Mn containing calcite grain
3.3. Possible manifestation of damage in the concrete microstructure

Having known the mineralogical properties of the flotation waste we have the possibility to predict the chemical reactions and weathering processes in a completed concrete structure.

3.3.1. Aggregate reaction

The iron sulphide containing concrete may show significant cracking of the aggregates. Generally most of the cracks originate from iron-sulfide containing regions within the aggregates and then extend into the cement paste. It appears that the degradation can be directly linked to the reaction of iron sulphides, which leads to an increase in volume within the aggregates that in turn crack and expand the concrete [11]. However some minor cracks in the aggregates caused by the iron sulfides particles might have been present in the aggregates before the concrete might be made originating from natural weathering. The investigated aggregates show ASR reactivity because of its high quartz content. The degree of reaction of the iron sulfides seems to be related to the position of the particles within the aggregates. Particles close to the surface of the aggregates show a higher degree of reaction than those near the center. It also looks like that some cracking of the aggregates along grain boundaries contributes to higher degrees of reaction, possibly by facilitating the ingress of oxygen. However, generally the extent of this reaction does not appear to be related to the position in the structure. For example in a dam concrete material particles in aggregates near to the surface of the dam did not appear to be more reacted than those far from the surface (even 3 to 4 m) inside [12].

Generally the specific volume increase of the degrading iron sulfides can be calculated and theoretically increase up to 1.3, respectively, 1.7 times. When it is assumed that the entire amount of iron sulfides degrades to half goethite (FeO(OH)) and half iron hydroxide [Fe(OH)₃], the maximum expansion of the aggregates can be calculated to be 0.07%. These critical expansion values might be larger than the intrinsic strain limits of the aggregates,
which are between 0.016% and 0.018% [13]. Beyond these critical values, the expansion starts to develop stress, which leads to cracks within the aggregates and finally cracks propagate into the cement paste. Thereby already small iron sulfide particles can provide enough stress to crack the aggregate in the concrete matrix. Iron sulfide degradation may be the main factor leading to the expansion in the concrete, but the possible secondary ettringite formation may contribute in a minor way to the degradation process. In general the expansion of the concrete is not homogeneous. The expansion of small inclusions inside aggregates may actually magnify the volume increase of the inclusions.

3.3.2. Secondary ettringite

Appearance of secondary ettringite crystals attributable to the release of sulfate from the iron sulfides inclusions might mainly form close to residual aluminate sources. These secondary ettringite deposits in the cement paste are typical for sulfate attack [14].

The ettringite formed in the microstructure, either from normal hydration or from the additional sulfate released from the iron sulfides, can be clearly identified in porous regions of the microstructure, mainly inside the shells left by hydrating grains. There is no evidence of distress around such deposits, however, even in systems where expansion due to internal sulfate attack is known to occur [4], these large deposits of ettringite are not believed to be the origin of expansion. Instead expansion is believed to arise from the reaction of submicroscopic crystals of calcium alumina monosulfate (monosulfate), within the C–S–H to form ettringite. The signature of expansion related to such internal sulfate attack is the formation of gaps around the aggregates as the expanding paste expands away from the nonexpanding aggregates. First the expansions are very low, so the predicted gaps would hardly be visible and secondly, it is likely that the aggregate is expanding. Due to these factors it is difficult to conclude about the contribution of ettringite formation from release of sulfates to the expansion of the concretes [12].

3.3.3. Thaumasite caused problems (TSA)

The thaumasite form of sulfate attack (often abbreviated to TSA) requires some kind of source of sulfate and also of carbonate. Thaumasite can occur rarely as a natural mineral as an alteration product of limestones. Thaumasite can form in concrete and in mortar. The cement hydration products normally present, mainly calcium silicate hydrate and calcium hydroxide are decomposed as a result of both sulfate attack and of carbonation. Since it is the calcium silicate hydrate in concrete that provides most of the strength, thaumasite formation results in severe weakening. Thaumasite has the chemical formula: \([\text{Ca}_3\text{Si(OH)}_6\cdot12\text{H}_2\text{O}](\text{SO}_4)(\text{CO}_3)\) or \(\text{CaSiO}_3\cdot\text{CaCO}_3\cdot\text{CaSO}_4\cdot15\text{H}_2\text{O}\). Thaumasite crystals tend to form at low temperatures, typically about \(4^\circ\text{C}–10^\circ\text{C}\). As it forms the concrete or mortar converts to a friable material. Concrete severely affected by thaumasite formation can easily be broken with the fingers and the coarse aggregate lifted out. A source of additional water is also required for thaumasite formation. Damp cementitious render over brickwork, especially where the render is cracked, and concrete and masonry in cool, damp cellars are typical examples of where thaumasite may occur. Normal sulfate attack usually results in the formation of ettringite. This uses aluminium provided by the cement and clearly this is limited in quantity in normal concrete. However thaumasite formation does not involve aluminium; given an adequate supply of sulfate and carbonate, thaumasite can continue to form until the calcium silicate hydrate is completely decomposed. Consequently
while the use of sulfate-resisting Portland cement provides some defence against normal sulfate attack, it does not give any particular protection against thaumasite formation. Sulfate in that case can be supplied from the sulfate content of the heavily oxidized parts of the tailing material. Carbonate can be supplied from the calcite and Ca-containing silicates present in the flotated tailing material. Serious damage to concrete or masonry due to thaumasite formation is not a common occurrence, even in cool, damp climates [15].

4. Conclusions

The Gyöngyössoroszi flotation tailing pond material contains quartz, pyrite, chalcopyrite, galena, sphalerite, calcite, and gypsum. The material of the waste is partly oxidized. From the point of view of concrete industry the material contains some problematic components. Firstly its high quartz content, because the material is able to cause alkali silica reaction. Secondly the oxidation of the pyrite grains would cause staining on the surface of the concrete, and every region of the concrete, where oxygen and moisture diffusion is high enough to support the oxidation process. The resulting secondary minerals, e.g. sulphates and ferri-oxi-hydroxides because of their larger volume would cause undesirable internal stresses. And in addition to these phenomena, the high sulphate content would cause secondary ettringite production. If the concrete would be placed in a cold and dump environment, the thaumasite formation could cause cracking and strength decreasing. It might be concluded that every kind of environment, where oxygen or water diffusion is confined seriously, e.g. dry internal parts of buildings or completely waterlogged underwater structures are proper application possibilities.

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