MŰEGYETEM 1782

BUDAPEST UNIVERSITY OF TECHNOLOGY AND ECONOMICS

INFLUENCE OF OZONE ON THE HARDENING OF CONCRETE

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Budapest 2017

Table of Contents

Table of Figures

1. Abstract

The work and the report of it, is aiming to verify and reproduce the findings patented in the United States of America under the registration number US20130033955A1. The part of the patent, which implies a possible increment of the relative strength of the hardened concrete when treated with ozonated water and mixed with cement and aggregate, is of interest. This promising attempt of improving the strength and durability was tested by comparison between 4 different mixtures of cement mortars. Two of them were mixed with ozonated water and 2 different ordinary Portland cements (OPC) of type CEM I (Hungarian and Austrian) respectively. The other 2 were mixed by using ordinary tap water and the same cements. Altogether 12 prism samples of the size 40x40x160 mm were produced and tested. After 7, 14 and 28 days one sample of each mixture was tested for flexural and compressive strength respectively. The results of the experiment in overall didn't show a significant change. Neither in the physical properties (consistency) of the mixtures by using ozonated water on the fresh mortar, nor on the mechanical properties of the hardened one. It can be concluded that for now the findings described in the part of this patent can't be reproduced by using OPC (type CEM I). There is a possibility of using different blended cements for the verification of the respective part of the patent. The dry mixtures were ensured by MC-Bauchemie Ltd.

2. Introduction

Concrete is by far the most used construction material in several fields in our present time. It would be pretty hard to imagine our modern society without it [2]. If the mechanical properties of the material could be so significantly improved by such a relatively simple method of using ozonated water for it, as it is described in the patent [1.], it would bear worldwide significance.

Ozone is formed from dioxygen by the action of ultraviolet light and also atmospheric electrical discharges in the nature, and is present in low concentrations throughout the Earth's atmosphere (stratosphere). In total, ozone makes up only 0.6 ppm of the atmosphere.[3]

From the patent it can be understood that from the process of ozone generation, unstable O_3 is created along with ions and radicals from the impurities of the charged water. Apparently these could help in strengthening the concrete. "Most of these components are unstable and quickly react with whatever suitable reactants are available to form more stable molecules. It is believed that the presence of ions in the charged water tends to interact with the cement and aggregate to accentuate the binding process carried out by the slurry mixture." Richard Sealy Clayton and his team (2013).

Concrete/cement mortar is basically composed of aggregate, cement and water. The aggregate is a mixture of coarse and fine rocks, in our case was sand of 0/4 fraction. [6] Cement is a mixture of gypsum, oxides of calcium, silicon and aluminum. As a binder we used two types of OPC (CEM I) from two different sources (Hungary and Austria). The dry mixture was ensured for us by MC-Bauchemie Ltd. for the tests. [4] And finally water is a key ingredient which allows the mixture to flow, set and harden after. The water/cement ratio is mainly responsible for the strength and durability of the cured mortar [5]. It is also very important to consider the amount of water since it's inversely proportional to the strength of the hardened mixture (Fig. 1.). As the water content increases, so does the porosity. On the other side, as in most parts of the world cement is the most expensive material for concrete, the quantity of this should be also taken into account.

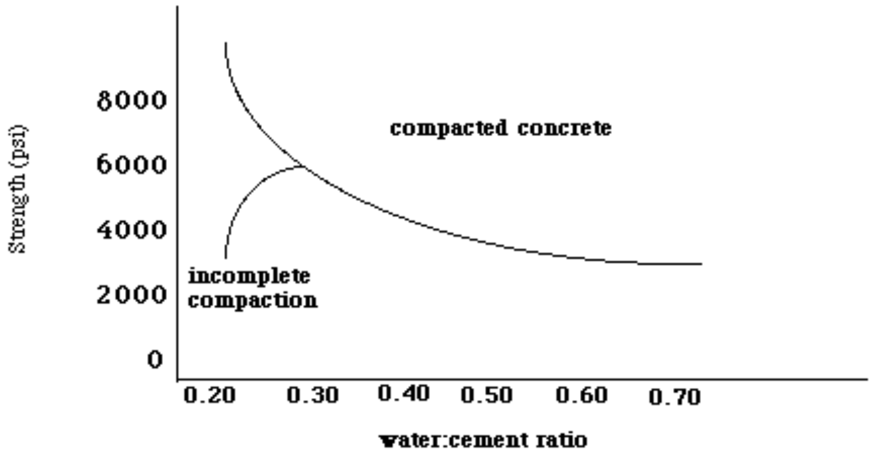

Figure 1.
Change in the strength of concrete against Water/cement ratio

With the knowledge that "In concrete, the single most significant influence on most or all of the properties is the amount of water used in the mix" (Jeffrey Girard 2011) [12]. It can be seen our big interest on searching new methods of strengthening concrete throughout the help of water. Therefore, if finding such a method without compromising the cost of the construction, economy could be boosted and more complex structures could be developed.

This study intends to prove quantitatively the results of mixing ozonated water with ordinary Portland cement. The results which have already been published in the patent US20130033955A1, imply an increment of almost two times the compressive strength of hardened concrete. For this reason, flexural and compressive strength tests will be carried out on cement mortar prisms to rectify the validity of the patented statement. And if in case any significant change is observed on the physical and mechanical properties of the fresh and hardened mortar, respectively; further and deeper understanding-study of the chemical process would be necessary.

3. Theory Reference

3.1. Ozone

Ozone's odour is sharp, reminiscent of chlorine, and detectable by many people at concentrations of as little as 100 ppb in air. Ozone's O_3 structure was determined in 1865. The molecule was later proven to have a bent structure and to be diamagnetic. In standard conditions, ozone is a pale blue gas that condenses at progressively cryogenic temperatures to a dark blue liquid and finally a violet-black solid. Ozone's instability with regard to more common dioxygen is such that both concentrated gas and liquid ozone may decompose explosively at elevated temperatures or fast warming to the boiling point.

Ozone is a powerful oxidant (far more than dioxygen) and has many industrial and consumer applications related to oxidation. This same high oxidising potential, however, causes ozone to damage mucous and respiratory tissues in animals, and also tissues in plants, above concentrations of about 100 ppb. This makes ozone a potent respiratory hazard and pollutant near ground level. However, the ozone layer (a portion of the stratosphere with a higher concentration of ozone, from two to eight ppm) is beneficial, preventing damaging ultraviolet light from reaching the Earth's surface, to the benefit of both plants and animals [3].

3.2. Concrete

The name “concrete” comes from the Latin “concretus” which means to grow together. The earliest stages of large scale concrete use, was documented from the ancient Romans, which allowed them to grow their empire widely with fast made and solid structures.

Concrete is a mixture of cement, aggregates and water that forms a fluid slurry that is easily poured and moulded into shape. The cement reacts chemically with the water to form a hard matrix that binds the components together into a durable stone-like material. Which has a relatively high compressive strength, but much lower tensile strength. For this reason, it is usually reinforced with materials that are strong in tension to provide tensile strength, yielding reinforced concrete.

3.3. Cement

Cement is a greyish binding powder that when mixed with water it sets, hardens and adheres to other materials. [7]

Hydraulic or non-hydraulic cement can be produced, depending upon the ability of the cement to set in the presence of water. In our experiments hydraulic cement was used, which is composed of four main components: Belite ($2CaO \cdot SiO2$);
Alite ($3CaO \cdot SiO2$);Tricalcium aluminate ($3CaO \cdot Al_2O_3$) and Brownmillerite
($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$). And two types of raw materials can be used for the production of cement:

- Marble, limestone, oyster shells, chalk, etc.
- Clay and clay-like materials such as chalk, slag from blast furnaces, bauxite, iron ore, silica, sand, etc.

3.4. Aggregate

Aggregates are granular materials of dimensions and properties suitable for use in civil engineering works. They can be classified taking into account the origin, the density and size of the fragments. The aggregate gives volume, stability, resistance to wear or erosion, and other desired physical properties to the finished product. [7]

Aggregate is the component of a composite material that resists compressive stress and provides bulk to the composite material. For efficient filling, aggregate should be much smaller than the finished item, but have a wide variety of sizes. For example, the particles of stone used to make concrete typically include both sand and gravel.

3.5. Mortar

Cement is used with fine aggregate to produce mortar for masonry, or with sand and gravel aggregates to produce concrete.

3.6. Flexural strength

The flexural strength is a material property, defined as the stress in a material just before it yields when performing a flexure test [8]. The transverse bending test is most frequently employed, in which a specimen having either a circular or rectangular cross-section is bent until fracture. It can be done by either according to ASTM C 293 (center point loading) or ASTM C 78 (third point loading), with results expressed in MPa.

[9]Many factors have been shown to influence the flexural tensile strength of concrete, particularly the level of stress, size, age and confinement to concrete flexure member, etc.

3.7. Compressive strength

Compressive strength is the capacity of a material to withstand loads tending to reduce its size [10]. It is measured by crushing cylindrical concrete specimens in a compression testing machine and calculated by the failure load divided with the cross sectional area resisting the load. The results are reported in MPa.

Compressive strength is a key value for design of structure since the results are primarily used to determine that the concrete mixture as delivered on site meets the requirements of the specified strength, in the job specification.

4. Methodology

In this research the hypothetic-deductive model was used as the way to approach the problem and find an answer to it. First the hypothesis of the influence of ozonated water in concrete, stated in the patent by Richard Sealy Clayton and his team was taken. Then through careful experimentation a couple of tests were run. After the results were studied a final conclusion could be reached.

4.1 Samples

For our experiments it was necessary to make two kind of dry mortar mixtures in our laboratory, one made with Hungarian CEM I and the other with Austrian CEM I OPC, in order to verify if the reaction could be generalized. In our samples the difference is shown as H-CEM I and A-CEM I respectively. A mixture for each cement with ozonated water and another control mixture with untreated water was prepared. Twelve samples of nominal size (40x40x160 mm) were needed in order to carry out the tests, three for each of the four different mix. From those twelve, one sample from each mixture was taken after 7, 14 and 28 days after being cured under lime water at a temperature of 20 ± 2^{o} C.

Since the focus of this report was to find the effectiveness of ozonated water on the mixture, the aggregate we used was the same throughout the experiment.

4.2 Instruments and process

During the experimentation, several instruments were used. Their different purposes helped throughout the process of making fresh mortar.

Prior the making of the mixture for the concrete, O_3 molecules had to be produced “on the spot” since they are very unstable and cannot be stored or transported. There are two main types of ozone generators, one is based on ultraviolet light of a certain wavelength, while the other is called corona discharge type. For our experiments we were using a commercial, tube type corona discharge ozone generator with a nominal capacity of 0,5 g/h O_3 generation (Fig. 2.).

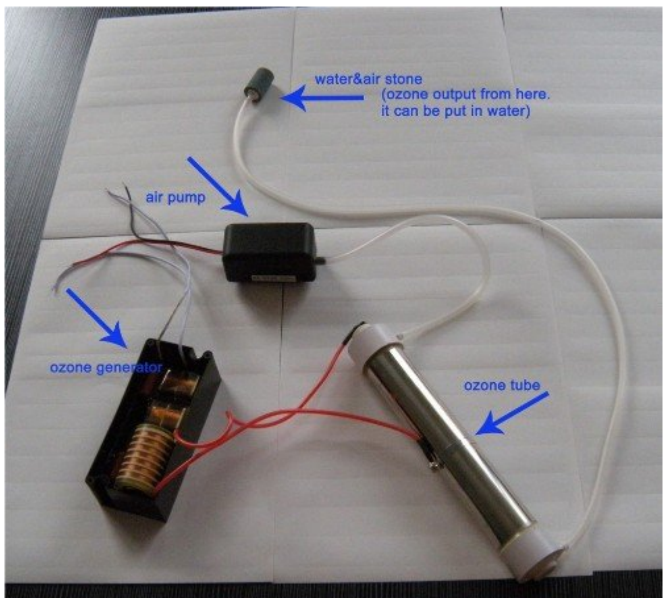

Figure 2. Ozone generator

Then through a diffuser we had bubbled O_3 into ordinary tap water at a rate of 3 litre/min. Which was produced from normal air for a period of 6 hours, and used the water immediately afterwards for mixing the mortar, since ozone decomposes in water very fast.

A special, standard automatic mixer for fresh mortar was used at the beginning for the mixing of water and the dry mixture (Fig. 3.).

Figure 3. Mortar mixer

Then a standard flow table (Fig. 4.) test was performed to determine the consistency of the mortar. The flow table would be dropped manually 15 times in order to spread the mixture. The diameter of the mortar patch was measured in two orthogonal directions. No difference in the consistency was found between the samples with O_3 and the ones without.

Figure.4 Flow table test

The mixes were placed in the moulds (Fig. 5.). Once the moulds were filled, they were compacted by a dropping table machine, being dropped 15 times automatically (Fig. 6.) and the surface smoothened.

Figure 5. Fresh mortar in the mould

Figure 6. Compacting table

After 24 hours, the samples were taken out of the mould to be cured under normal water (Fig. 7.). After 7, 14 and 28 days the flexural and compressive strength of the samples were tested by a machine (Fig. 8-9.).

Figure 7. Curing of samples

5. Experimental Work

5.1 Flexural strength test

The flexural strength is a measure of the tensile strength of mortars. This test allows us to measure the strength before failure in bending, in this case of 40x40x160 mm unreinforced mortar prisms. The center-point loading method was used for this research.

After 7, 14 and 28 days of curing the samples were first weighted and the sides measured. Then placed on top of the supports of the hydraulic press and loaded afterwards.

Figure 8. Bending test

Figure 9. Bending test after loading

5.2 Compressive strength test

The compressive strength test is the most common method nowadays among engineers, to measure the performance of stone like materials. It can be done by compressing either cylindrical or cubic specimens until failure.

In our case the tests were carried on the halves of the specimens remaining after the flexural test. Each half would be transferred to another hydraulic press, placed between two aligned solid metal plaques of 40x40 mm and loaded until failure (Fig. 9.).

Figure 10.
Compressive strength
test

6. Test results

6.1 Flexural strength results

The results from the carried out experiments are shown below. These tables show the results of the flexural strength tests after 7, 14 and 28 days respectively (Table 1-3.).

		mm	mm	mm	g	N	kg/m^3	N/mm^2
Mixture	Type	Side 1	Side 2	Width	Weight	Force	Density	Flex. Strength
1	225ml H_2O +O_3; H-CEM I	40.16	40.35	159.96	578	1357	2230	3.11
2	200ml H_2O +O_3; A-CEM I	40.75	40.67	160.58	586	2328	2202	5.18
3	225ml H_2O; H-CEM I	40.32	40.07	159.74	579	1515	2243	3.51
4	200ml H2O; A-CEM I	40.67	40.12	160.81	589	2447	2245	5.61

Table 1. Flexural strength after 7 days

		mm	mm	mm	g	N	kg/m^3	N/mm^2
Mixture	Type	Side 1	Side 2	Width	Weight	Force	Density	Flex. Strength
1	225ml H_2O +O_3; H-CEM I	40.90	40.10	160.10	583	1955.00	2220	4.46
2	200ml H_2O +O_3; A-CEM I	40.70	40.00	161.00	577	2254.00	2185	5.15
3	225ml H_2O; H-CEM I	41.00	40.20	159.90	576	2002.00	2202	4.57
4	200ml H_2O; A-CEM I	40.90	40.90	161.10	589	2369.00	2186	5.19

Table 2. Flexural strength after 14 days

		mm	mm	mm	g	N	kg/m^3	N/mm^2
Mixture	Type	Side 1	Side 2	Width	Weight	Force	Density	Flex. Strength
1	225ml H_2O +O_3; H-CEM I	40.35	40.22	160.04	580	1941.00	2233	4.46
2	200ml H_2O +O_3; A-CEM I	40.87	40.14	160.93	583	2387.00	2208	5.44
3	225ml H_2O; H-CEM I	40.59	40.26	159.69	586	2058.00	2246	4.69
4	200ml H_2O; A-CEM I	40.12	40.51	160.88	586	2176.00	2241	4.96

Table 3. Flexural strength after 28 days

6.2 Compressive strength test results

The following tables show the results of the compressive strength tests after 7, 14 and 28 days respectively (Table 4-6.).

		mm	mm	mm	g	kN		Density	N/mm^2
Mixture	Type	Side 1	Side 2	Width	Weight	Force		Density	Compr. Strength
1	225ml H_2O +O_3; H-CEM I	40.16	40.35	159.96	578	37.14	42.69	2230	24.95
2	200ml H_2O +O_3; A-CEM I	40.75	40.67	160.58	586	52.05	56.74	2202	34.00
3	225ml H_2O; H-CEM I	40.32	40.07	159.74	579	42.7	41.58	2243	26.34
4	200ml H_2O; A-CEM I	40.67	40.12	160.81	589	56.23	54.65	2245	34.65

Table 4. Compressive strength after 7 days, where the strength values were calculated by using the sizes of the compressive plate which were 40x40mm.

		mm	mm	mm	g	kN		Density	N/mm^2
Mixture	Type	Side 1	Side 2	Width	Weight	Force		Density	Compr. Strength
1	225ml H_2O +O_3; H-CEM I	40.90	40.10	160.10	583	53.01	52.58	2220	33.00
2	200ml H_2O +O_3; A-CEM I	41.00	40.00	161.00	577	62.96	63.00	2185	39.36
3	225ml H_2O; H-CEM I	40.70	40.20	159.90	576	49.96	51.21	2202	31.62
4	200ml H_2O; A-CEM I	40.90	40.90	161.10	589	62.27	65.15	2186	39.82

Table 5. Compressive strength after 14 days, where the strength values were calculated by using the sizes of the compressive plate which were 40x40mm.

		mm	mm	mm	g	kN		Density	N/mm^2
Mixture	Type	Side 1	Side 2	Width	Weight	Force		Density	Compr. Strength
1	225ml H_2O+O_3; H-CEM I	40.35	40.22	160.04	580	57.00	60.27	2233	36.65
2	200ml H_2O+O_3; A-CEM I	40.87	40.14	160.93	583	65.36	61.47	2208	39.63
3	225ml H_2O; H-CEM I	40.59	40.26	159.69	586	53.53	58.14	2246	34.90
4	200ml H_2O; A-CEM I	40.12	40.51	160.88	586	65.97	67.18	2241	41.61

Table 6. Compressive strength after 28 days, where the strength values were calculated by using the sizes of the compressive plate which were 40x40mm.

6.3 Tests analysis

It can be clearly seen that under the described conditions, there’s no significant change between the specimens which were mixed with ozonated water and the ones that were not. We must mention that we also did not experience change in the consistence of the freshly mixed mortar prepared with ozonated water if compared to ordinary tap water. The difference in the amount of mixing water only due to the different cements, having different water demands.

7. Conclusions

As mentioned before, improving the compressive strength of concrete could bring numerous advantages and growth in the industry.

This report is intended to verify the statements related to the positive effect of ozonated water in the strength of concrete production, as mentioned in the patent **US20130033955A1.** However, such results couldn’t be replicated in this study.

The approach of how the experiments were done, does not create sufficient criteria to validate or invalidate the results of the patent. It is advised to increase the number of specimens to at least three samples per every different cured mixture. To be able to have a higher accuracy and heavier proof for validation.

In addition, if repeating the experiments by using different blended cements, this might lead to a positive result. Since we knew that the type of cement used in the United States contained Fly Ash in 5-10 mass% [12.], for this time it was only intended to make the experiments with regular cement (no special additives) and if no positive results were found, then consider the reaction that might lead other components such as the fly ash.

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FIGURES

- FIG 1. https://qph.ec.quoracdn.net/main-qimg-76f8566693df379d188285bee17d38c1. Accessed on June 25th 2017.
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