



XRD AND TGA INVESTIGATION OF HARDENED CEMENT PASTE DEGRADATION

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Abstract: It is generally recognized that the environmental degradation of the concrete infrastructure is a serious, large scale and costly problem in many parts of the world. In this paper a deterioration of concrete by leaching of hardened cement paste due to aggressive water action is considered.

Concrete from a hydro-electric power plant's pipeline 30 years old was characterized with X-ray diffraction (XRD), and thermogravimetric analysis (TGA/DTA). The study highlights the capabilities of the methods for the analysis of concrete towards the determination of hardened cement paste degradation. On the basis of a visual survey of drilled cores, a number of representative spots were selected for detailed testing and verification of visual estimates.

The methods ascertain a leach of hardened cement paste on samples taken from a surface concrete cover layer of few millimetres, and from flaws like cracks, segregations or cold joints. On these samples XRD results showed small quantity of ettringite, calcium carboaluminate hydrate and Friedel's salt, and a complete leach of portlandite, while TGA results indicated small quantities of hydrates. Samples taken from flawless inside of concrete layer showed expected quantities of hydrates for the concrete.

Keywords: X-ray diffraction, thermogravimetric analysis, concrete, degradation.

1 Introduction

Contrary to common belief, concrete is a complex composite material, whose structure and properties can change over time. It is generally recognized that the environmental degradation of the concrete infrastructure is a serious, large scale and costly problem in many parts of the world. The concrete structures are designed and built for a service life, which is defined by the designer and is controlled by the manufacturer. For this period of time, the structure should not be so deteriorated that it does not fulfill any more its functions. In this paper a deterioration of concrete by leaching of hardened cement paste due to aggressive water action is considered.

Waters which are acid owing to the presence of organic acids and carbon dioxide do not normally produce more than a surface attack on mass Portland cement concrete, though with the more acid waters over long period of years the action may penetrate to a depth of few centimeters. If, however, there exists a considerable hydrostatic pressure tending to force the water through a concrete mass the action may become much more serious. The destructive effect on thin-walled concrete products like pipes may also be severe.

Pure water dissolves lime to the extent of about 1.2 g/L and is also capable of leaching out lime from set cement compounds. When carbon dioxide is present in the water in a free state it increases the aggressive action of the water. Initially it reacts with the lime to form insoluble calcium carbonate, but on further action the much more soluble calcium bicarbonate is formed. A solution of calcium bicarbonate alone in water will not dissolve further quantities of calcium carbonate, and if it reacts with lime the insoluble calcium carbonate is formed [2].

In water conduits built in Scotland in connection with a hydro-electric power scheme [2] was found that the surface of the concrete became attacked and the aggregate exposed within less than one year's exposure to waters of an average pH of about 6.8. After a period of years the coarse aggregate near the surface became loose and commenced to be washed out. In other constructional work on similar schemes in Scotland a lining of calcium aluminate cement concrete has been applied to aqueducts and pressure tunnels. Pozzolanic cements, and some Portland blastfurnance cements, are rather more resistant to attack than Portland cement, but concretes made with them still suffer gradual surface erosion when exposed to running water, or leaching if the concrete is permeable.

Considerable trouble has been experienced in the Scandinavian countries with large concrete dams exposed to pure or acid mountain waters [2]. A dam is subjected to a one-sided pressure by water and, if the concrete is permeable, water will continuously permeate through the mass. With waters which are not very pure and have little solvent action the pores in a concrete mass often slowly seal up, but when the water has a marked solvent action lime is gradually removed from the concrete which becomes progressively more porous.

Concrete pipes and similar thin-walled concrete units require rather special consideration in regard to their resistance to chemically destructive agents.

Particular attention has been paid in Sweden to the attack of concrete pipes by acid waters containing free carbon dioxide [2]. Concrete pipes of sound quality could be used, it was concluded, unless the subsoil water had a very low content of bicarbonates of lime and magnesia (a very low temporary hardness), or had a rather high content of aggressive carbonic acid, and the circulation of the water at the same time was considerable [2].

In this paper 30 years old concrete from a pipeline that leads water from a reservoir (lake) to the turbine of the hydro-electric power plant was characterized with X-ray diffraction (XRD), and thermogravimetric analysis (TGA/DTA). The study highlights the capabilities of the methods for the analysis of concrete towards the determination of hardened cement paste degradation.

2 Sample preparation

Firstly, a visual survey of the pipeline water conduits in connection with a hydro-electric power scheme was conducted with categorization of flaws on the basis of outward appearance and samples were taken drilling a core, **Figure 1 - 4**. On the basis of a visual survey of drilled cores, a number of representative spots were selected for detailed testing and verification of visual estimates. Samples were taken from a *surface* concrete cover layer of few millimetres, and from flaws like *cracks*, *segregations* or *cold joints*. Samples were taken from these representative spots by carefully scraping and drilling concrete in powder. Powder samples were stored in sealed bags to prevent carbonation. Before analyses powder was additionally grind in corundum crucible.

3 Thermogravimetric analysis

Eight samples were analyzed by thermogravimetric analysis (TG/DTA). The samples were taken in a ceramic crucible and heated from room temperature to 950 °C in thermoanalyzer TG – 50 Mettler (procesor TC 11, TA 4000) at a heating rate of 10 °C min⁻¹ using air as a medium under static condition. Alumina powder was used as the reference material. TG and DTA were done simultaneously. The samples were dried at 105 °C in oven and cooled to room temperature before performing TG/DTA analysis.

Table 1. TG/DTA results for four characteristic samples.

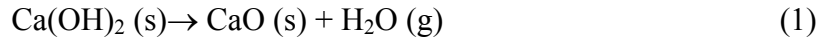
Sample	Temperature range (°C)	Peak temperature (°C)	Weight loss (%)
<i>Flawless</i> <i>10+375</i> <i>D=24</i>	29 - 100	35	0,72
	100 - 350	138	2,37
	400 - 460	431	0,74
	506 – 896	805	33,17
<i>Surface</i> <i>0+210</i>	26 - 80	38	0,86
	82 - 400	365	4,41
	400 - 496	445	0,46
	496 - 892	779	36,73
<i>Segregation</i> <i>3+342</i>	28 - 100	36	1,01
	520 - 860	799	41,79
<i>Crack</i> <i>0+250</i>	25 -99	42	0,95
	100 - 210	105	0,25
	450 - 857	800	35,16

Table 2. Ca(OH)₂ and CaCO₃ estimated by TG/DTA.

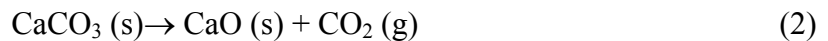
Sample	Ca(OH) ₂ (%)	CaCO ₃ (%)
<i>Flawless 0+375</i> <i>D=24</i>	0,49	75,34
<i>Surface 0+210</i>	0,23	83,42
<i>Segregation 3+342</i>	0	94,95
<i>Crack 0+250</i>	0	79,91

The total weight losses of samples due to heating from 25 °C to 950 °C were between 40 % and 47%. The TG/DTA results are presented in **Table 1**, as weight loss with respective temperature range and peak temperature for the four characteristic samples. The four characteristic

endothermic effects are noticed. The first effect, in temperature range from 25 to 100 °C is due to evaporation of surface adsorbed water because samples adsorbed water from air during its cooling to the room temperature after drying at 104 °C. The second endothermic effect, in temperature range from 100 to 350 °C, is attributed to the dehydration of C–S–H and ettringite and calcium aluminate hydrate [1]. The temperature at which these compounds lose water depends upon the available CaO:SiO₂ ratio in the hydrated cement matrix. The third effect, with peak temperature between 430 i 460 °C, indicates the decomposition of Ca(OH)₂ formed during hydration. The Ca(OH)₂ was estimated from the weight loss measured from the TG curve between the initial and final temperature of the corresponding TG peak by considering the following decomposition reaction (**Table 2**):



Finally, an endothermic around 790 °C indicates the decarbonation of calcium carbonate in the hydrated compound. The CaCO₃ was estimated from the weight loss by considering the following decarbonation reaction (**Table 2**):



It can be seen from **Table 1** that ettringite, C-S-H gel and calcium aluminate hydrate are not present in sample *Segregation 3+342*. Ettringite, C-S-H gel and calcium aluminate hydrate are present in small quantity in sample *Crack 0+250*, whereas they can be found in more quantity in samples *Flawless 10+375 D=24* and *Surface 0+210* (**Table 1**). Moreover, it is evident from **Table 2**, that calcium hydroxide is not present in samples *Segregation 3+342* and *Crack 0+250*.

4 X-ray diffraction analysis

The powder method of X-ray diffraction was adopted in the present study. For this, a Phillips diffractometer PW1730 with a X-ray source of Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) was used. The scan step size was 0.02°, the collection time 1s, and in the range 2 Θ CuK α from 5 ° to 50(65)°. The X-ray tube voltage and current were fixed at 40 kV and 30 mA respectively.

Although X-ray diffractometry does not provide any reliable quantitative information, the technique is sensitive. An on-line search of a standard database (JCPDS database) for X-ray powder diffraction pattern enables phase identification for a large variety of crystalline phases in a sample [3].

Figure 1 – 4 illustrate the XRD diffractograms for investigated samples. Each figure presents comparatively diffractograms of a sample taken from a *flawless* concrete spot (black top line) and a *surface* concrete cover layer of few millimeters, or from flaws like *cracks*, *segregations* or *cold joints* (green bottom line). The symbols on figures indicate the positions and peak intensities of the powder diffraction standard from JCPDS database. In samples *Flawless 3+342* and *Segregation 3+342*, **Figure 1**, XRD analysis indicates predominance of calcite [CaCO₃] and dolomite [CaMg(CO₃)₂] peaks. In both samples Quartz [SiO₂] is identified.

In sample *Flawless 3+342* diffraction peaks indicate presence of portlandite [Ca(OH)₂], ettringite and carboaluminate hydrate and Friedel's salt (overlap near 2 $\Theta = 11$ °). However, sample *Segregation 3+342* shows no diffraction peak of portlandite [Ca(OH)₂], and small quantity of ettringite, calcium carboaluminate hydrate and Friedel's salt (chloroaluminates) is identified.

In samples *Flawless 10+375* and *Crack 10+375*, **Figure 2**, *Flawless 10+250* and *Crack 10+250*, **Figure 3**, *10+210 D=11cm* and *Surface 10+210*, **Figure 4**, XRD analysis indicates

predominance of calcite $[CaCO_3]$ peaks. In all *Flawless* samples diffraction peaks indicate presence of portlandite $[Ca(OH)_2]$, ettringite and carboaluminate hydrate and Friedel's salt. However, in both *Crack* samples and sample *Surface* XRD analysis shows no diffraction peak of portlandite $[Ca(OH)_2]$, and small quantity of ettringite, calcium carboaluminate hydrate and Friedel's salt is identified. In all samples small quantity of Quartz $[SiO_2]$ is identified.

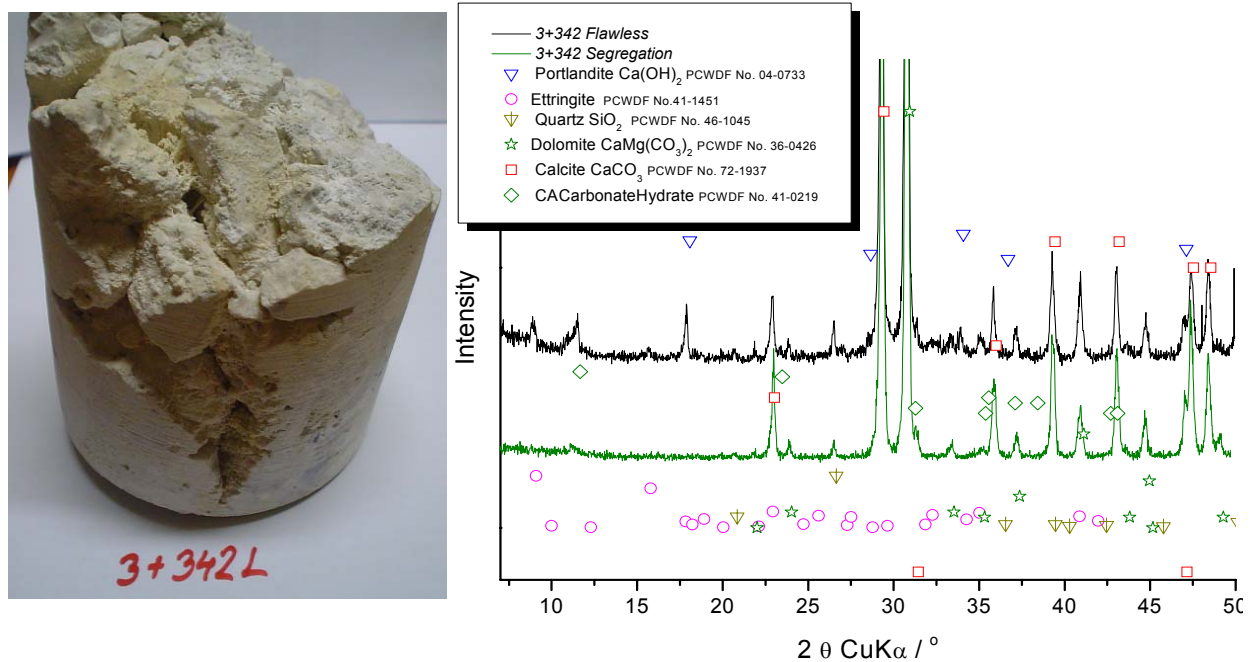


Figure 1. Photo and XRD diffractograms for samples *Flawless 3+342* and *Segregation 3+342*.

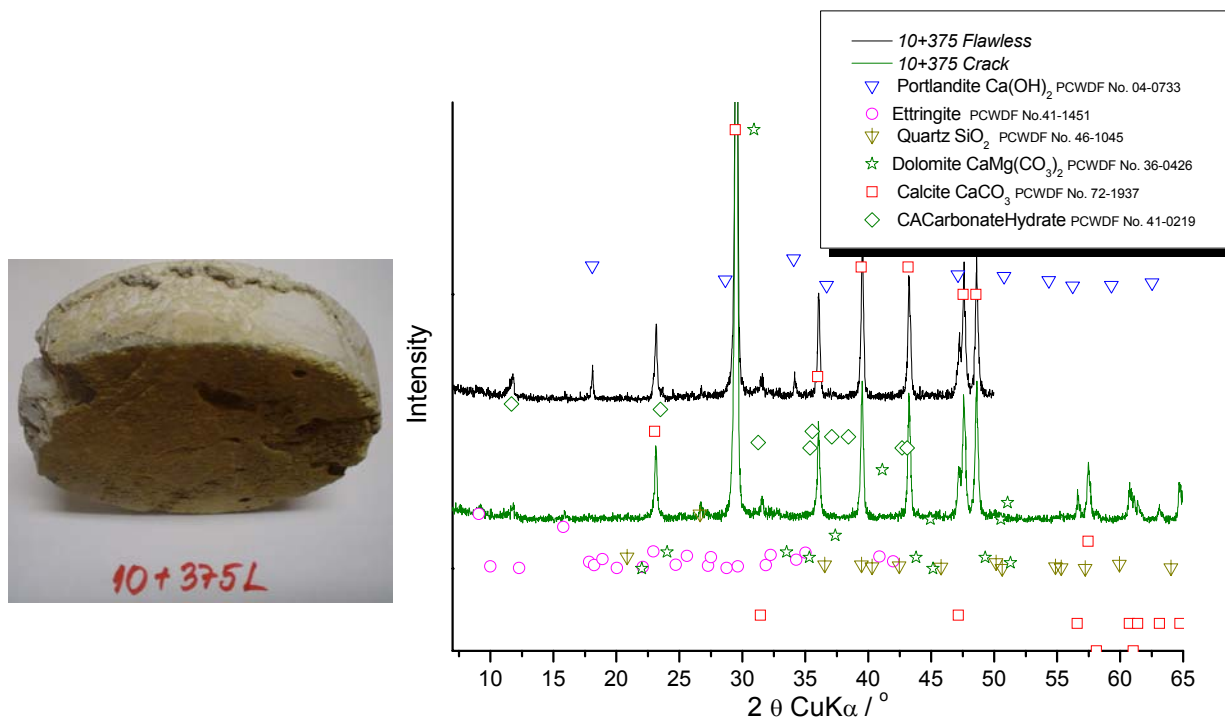


Figure 2. Photo and XRD diffractograms for samples *Flawless 10+375* and *Crack 10+375*.

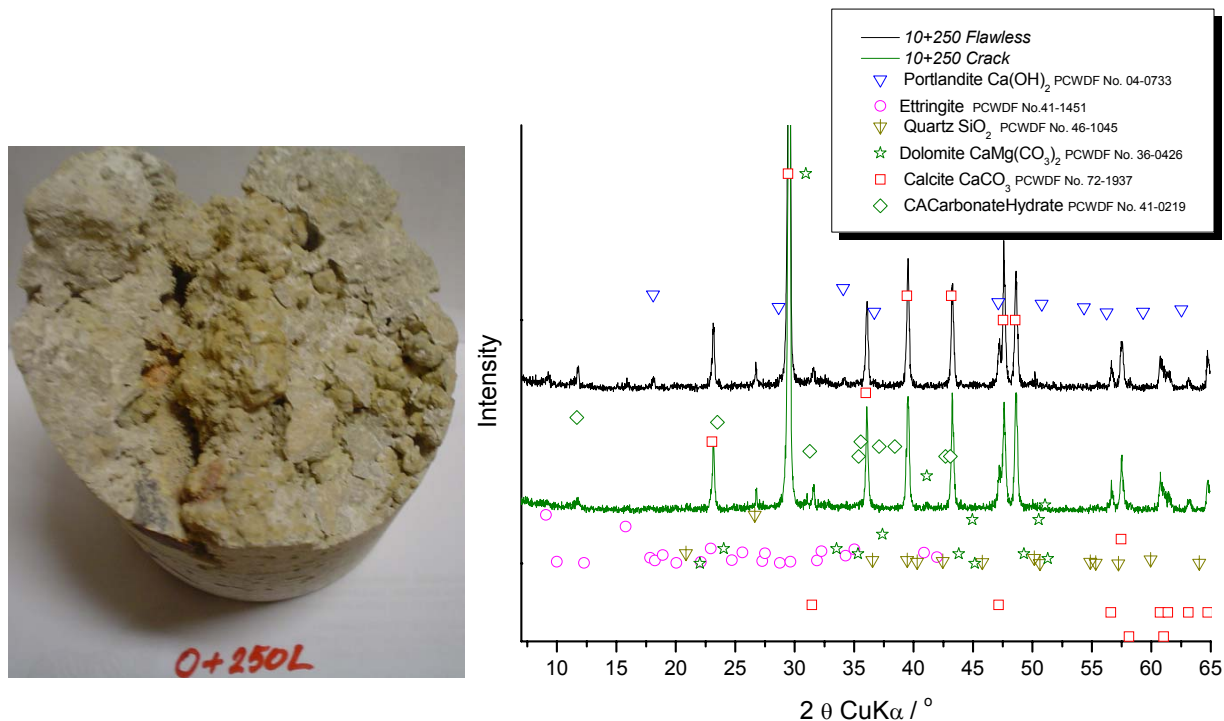


Figure 3. XRD diffractograms for samples *Flawless 10+250* and *Crack 10+250*.

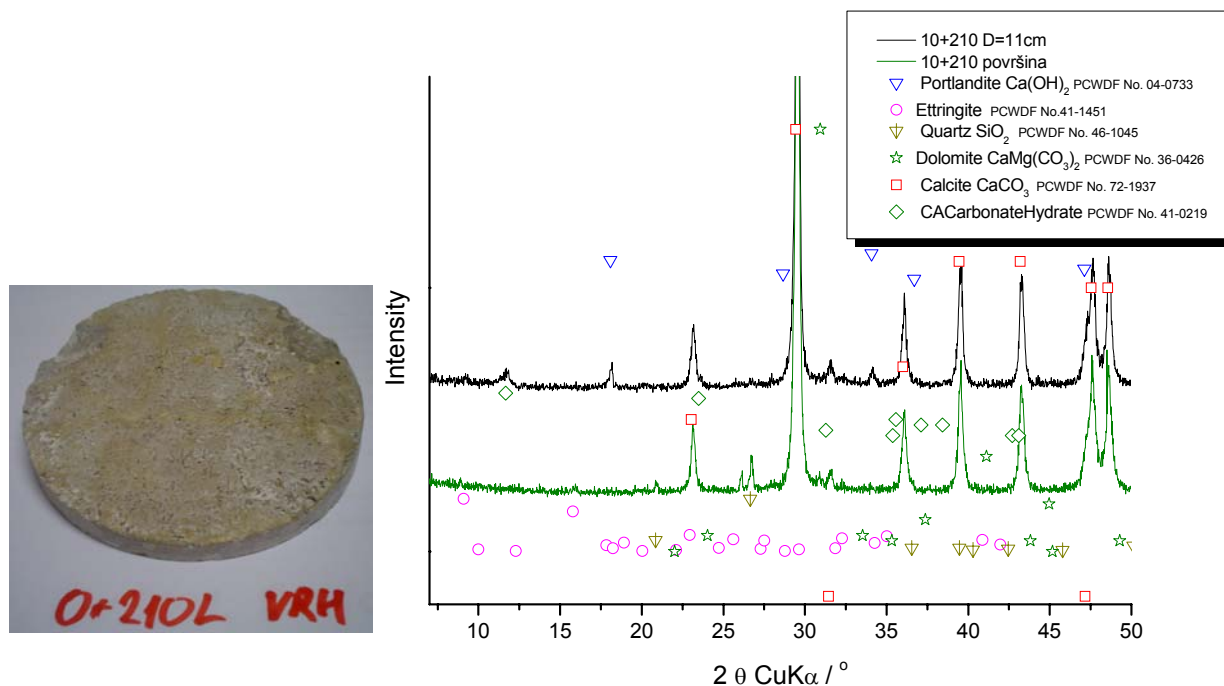


Figure 4. Photo and XRD diffractograms for samples *10+210 D=11cm* and *Surface 10+210*.

5 Conclusion

Concrete from a hydro-electric power plant's pipeline 30 years old was characterized with X-ray diffraction (XRD), and thermogravimetric analysis (TGA/DTA). The study highlights the capabilities of the methods for the analysis of concrete towards the determination of hardened cement paste degradation. The methods ascertain a leach of hardened cement paste on samples taken from a surface concrete cover layer of few millimetres, and from flaws like cracks,

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6 References

1. Vedalakshmi R., Sundara Raj A., Srinivasan S., Ganesh Babu K.: Quantification of hydrated cement products of blended cements in low and medium strength concrete using TG and DTA technique, *Thermochimica Acta* 407, 49–60, 2003.
2. F.M. Lea, *The Chemistry of Cement and Concrete*, 3rd Ed., Edward Arnold, London, 1970. ISBN: 0-7131-2277-3
3. V.S. Ramachandran, *Thermal Analysis*, in: *Handbook of analytical techniques in concrete science and technology*, V.S. Ramachandran and J.J. Beaudoin, Eds., Noyes Publications, New Jersey, 2001. ISBN: 0-8155-1437-9