

REUSE OF CONCRETE WASTE: CHALLENGES WITH HEXAVALENT CHROMIUM (Cr⁶⁺)

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ABSTRACT

In cooperation with the Norwegian environmental Authorities, the Norwegian Geotechnical Institute (NGI) is currently carrying out a project to investigate the environmental fate and speciation of hexavalent chromium (Cr(VI)) released from concrete waste under realistic reuse scenarios. A leaching test was conducted using chromium-contaminated concrete mixed with sand, which was subjected to end-over-end agitation for 24, 96 and 168 hours. The results showed that all of the chromium in the concrete was leached as Cr(VI). This was mainly because of the high pH of 12 that persisted throughout the whole test period. Leaching tests with different types of soils are to be carried out to investigate the effect of total organic carbon (TOC) and pH on leaching of Cr(VI). Furthermore, kinetic tests to study the oxidation rate of Cr(VI) to the less toxic Cr(III) will be performed. The work also considers analytical issues as well as an investigation of the chemical composition of “clean” concrete obtained from cement producers. Results from the study will be presented. One known analytical difficulty is related to deciding which method should be used to analyze Cr(VI) in concrete as well as how results can vary between different laboratories. The results showed great variation in both analyzing methods and laboratories.

KEYWORDS

Concrete, Hexavalent chromium, Re-use, Analytical method, Metals in concrete, Cr(VI) in concrete

INTRODUCTION

The European Commission's Circular Economy Action Plan includes a legislative proposal on waste and provides long-term targets to reduce landfilling and increase recycling and reuse (European Commission, 2015). One of the goals set out in the Action Plan is to achieve a 70 % reuse of materials in building and construction projects. Concrete is a large fraction related to demolition waste from building and construction projects. Together with brick waste, concrete makes up approximately 22 % of the waste disposed of at Norwegian landfills (Statistics Norway, 2017). Chromium is naturally present in cement materials as the raw material used is limestone, different fuels are used in clinker production and cement and concrete contain different additives (Butera et al. 2014). This chromium could be released as Cr(III) or Cr(VI) depending on different environmental factors. Cr(VI) is hazardous for both the environment and human health and thus represent an environmental problem.

To reduce the amount of concrete waste sent to landfills, the Norwegian Environmental Authorities have proposed guidelines to support the reuse of this waste fraction. The guideline includes threshold values (concentrations in solid samples) for chromium (total) and the much more toxic hexavalent chromium (Cr(VI)). In reality, when samples are taken from projects generating concrete waste, concentrations of Cr(VI) often exceed the threshold value. This leads to the concrete being disposed of at a landfill rather than being reused. At high pH, which is the case in concrete, chromium often occurs in the hexavalent form. However, knowledge related to the fate of leached Cr(VI) that comes in to contact with water and migrates further into the environment is scarce. The fate of Cr(VI) in the environment depends on several different reactions with soil compounds such as precipitation, sorption and complexation, all of which can affect the mobility and availability of Cr(VI) (Butera et al. 2015).

Jung et al. 2014 looked at the leached Cr(VI) concentration from concrete exposed to liquid with different pH. Results showed that an increase in acid resulted in a gradual increase in the Cr(VI) concentration until the HCL acid concentration reached 2 mg/L. Further addition of HCL dramatically reduced Cr(VI) concentration (Jung et

al. 2014). The aim of this project is to investigate the speciation of Cr(VI) released from concrete waste in realistic re-use conditions and to see how Cr(VI) in the leachate is affected by changes in pH.

In addition, chemical analysis of Cr(VI) is challenging, where different standard methods for solid samples, give large variation in results. This makes the decision of reuse versus landfilling somewhat haphazard, and we see that this lack of knowledge prevents reuse of concrete. This project will try to assess the analytical challenges and come to a best practice recommendation.

1. MATERIALS AND METHODS

1.1. Leaching test with concrete and sand

Concrete samples were taken from an old factory in Rjukan, southeast Norway. The concrete is approximately 80 years old. The leaching test was conducted according to NS-EN-12457/1-3.

The concrete was crushed to a fraction of ≤ 2 mm and mixed with sand with low organic content (TOC) at an 80/20 percent ratio. Water was added in a L/S ratio of 10. The samples was subjected to end-over-end agitation for 24, 96 and 168 hours. Before filtration, the samples was stationary for 24 hours to allow sedimentation of the particles. The samples was filtered with a 0,45 μm filter. A conservation agent ((NH_4) 2SO_2 + NH_4OH) was added to leachate to be analyzed for Cr(VI) before being sent to an external lab for analyzation.

Analytical methods used were EPA 200.7, ISO 11885, CSN EN 16192, EPA 6010, SM 3120 for Cr-total and CSN EN 16192, EPA 7199, SM 3500-Cr for Cr(VI).

1.2. Ring test

Concrete samples from Rjukan, southeast Norway were sent to two different laboratories for analysis of total-Cr and Cr(VI). The sample had previously been analyzed using the method MST REFLAB 2000 for analysis of dissolved Cr(VI). This method gave a results of 0.71 mg/kg Cr(VI). Two samples of the same sample material were sent to each of the laboratories. One of the samples was crushed and prepared by NGI, the other was a concrete sample to be prepared by the laboratories (Table 1). The sample that was prepared by NGI was crushed with a jaw crusher and a ball mill to a fraction of ≤ 250 μm . The sample material was well mixed and split into two samples of 200 g. The concrete sample to be prepared by the laboratories was split into two parts of 433 g using a rock saw (Table 1).

Table 1. Ring test sample overview

Sample	Preparation	Fraction	Amount of sample	Parallels	Method
Concrete	NGI	≤ 250 μm	200 g	4	ISO EN15192
Concrete	Laboratories	See ISO EN15192	433 g	4	ISO EN15192

2. RESULTS

2.1. Leaching test with concrete and sand

Analysis of the concrete used in the study showed a concentration of 7.3 mg/kg Cr(VI) (using method ISO EN15192) which is above the national limit for reuse of concrete in Norway of 2 mg/kg Cr(VI). Cr(VI) concentrations in the leachate water over time are reported in Figure 1. All samples retained high pH of 12 even when mixed with sand. The pH was not affected with time. All of the total-Cr in the samples was leached as Cr(VI) and the leaching increased with time.

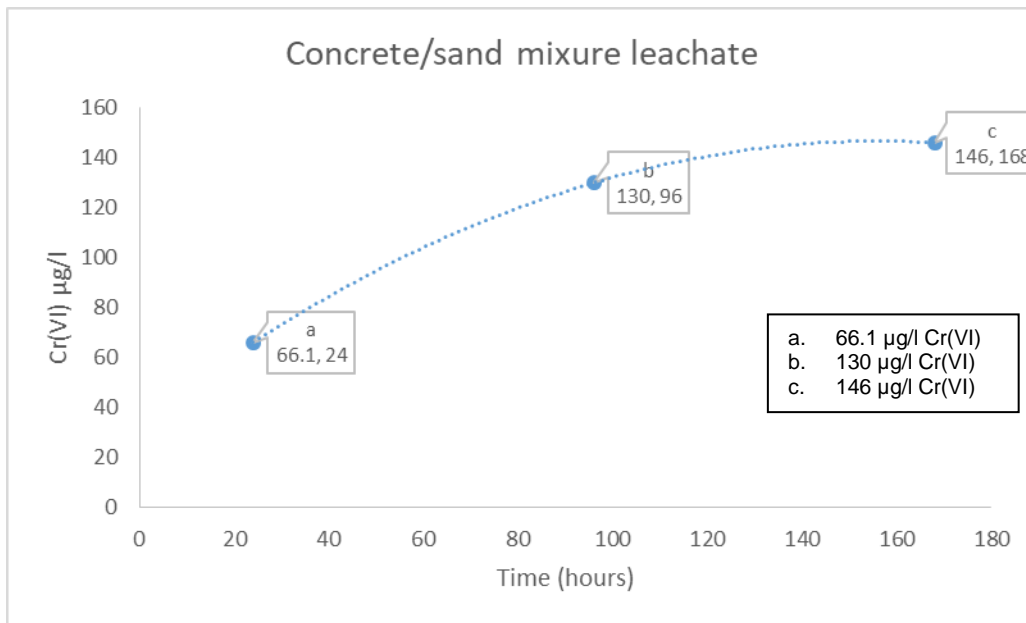


Figure 1. Concentration of Cr(VI) in leachate water from concrete mixed with sand over time. The samples was subjected to end-over-end agitation for a) 24 hours, b) 96 hours and c) 168 hours.

2.2. Ring test

Analytical data from the ring test are reported in Figure 2 and Figure 3. Figure 2 shows the Cr(VI) concentration in the concrete that was prepared by NGI. Figure 3 shows the Cr(VI) concentration in the concrete that was prepared by the laboratories. The analysis was carried out in four replicates. For the sample prepared by NGI, lab 2 reported consistently higher concentrations. For the sample prepared by the laboratories themselves, lab 1 showed consistently higher concentrations.

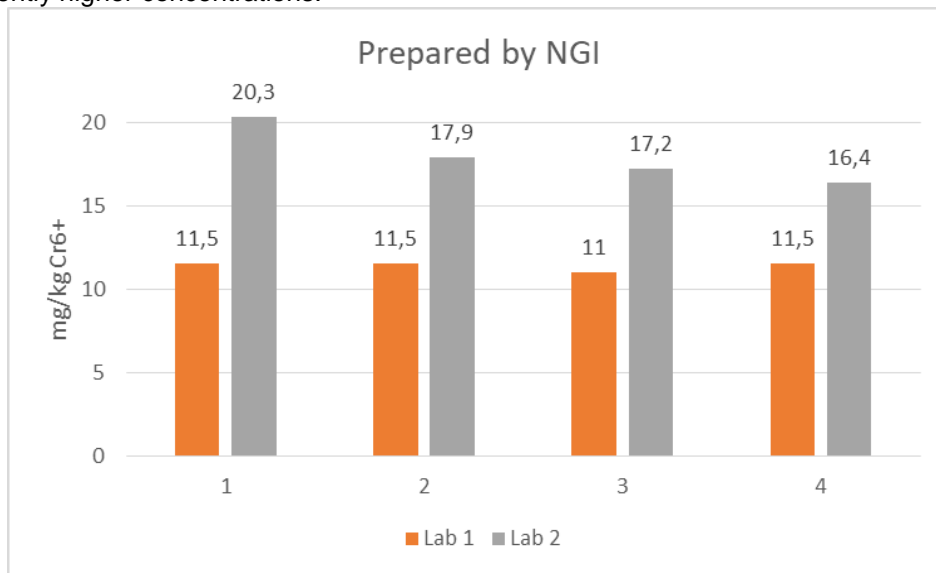


Figure 2. Analyzed concentration of Cr(VI) in concrete samples from Lab 1 and Lab 2 prepared by NGI with a fraction of $\leq 250 \mu\text{m}$.

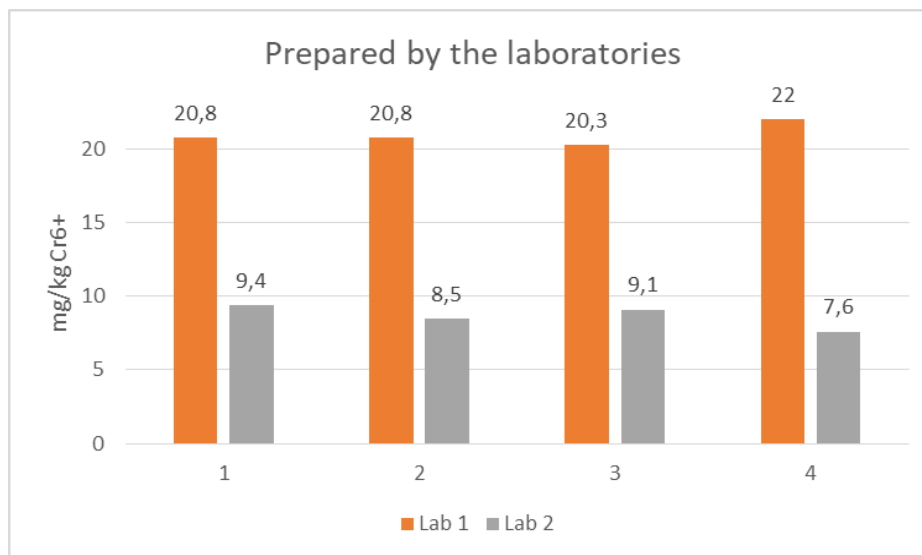


Figure 3. Analyzed concentration of Cr(VI) in concrete samples from Lab 1 and Lab 2 prepared by the laboratories.

3. CONCLUSIONS

The leaching test showed that sand had no buffering capacity against the high pH of the concrete. In addition, the pH did not change over time. With the high pH in the leachate water, all of the chromium in the concrete was leached as Cr(VI) and the Cr(VI) concentration increased over time. The biggest increase in concentration was from one to four days of agitation, with a slight increase from four to seven days of agitation. This implies that to obtain a realistic picture related to leaching from concrete a time period of at least four days should be used in leach tests. Jung et al. 2014 studied the immobilisation of Cr(VI) ions in cement matrix. After a cement hydration for 28 days, the water-soluble Cr(VI) decreased from between 12.3 to 19.0 mg/kg-cem to approximately 2.9 mg/kg-cem. Jung et al. 2014 believe this is due to a physical adsorption of Cr(VI) ions in the cement matrix. The results reported here point to the need for longer term kinetic tests to find the point at which leaching from concrete ceases. This will provide a better understanding of the fate of Cr(VI) in the environment. The same test should also be carried out using different types of soils and concrete mixtures.

The ring test shows low variation between analytical replicates, but high variation between the results from the two different laboratories. This points to the fact that obtaining a representative sample for analysis is very difficult. Concrete is inherently heterogeneous and this will affect certainty within chemical analysis. The focus of the ring test was not to assess different analytical methods, so the same method was used for all of the chromium analyses. However the concentration of 0.71 mg/kg Cr(VI) obtained using MST REFLAB 2000 method was ten times lower than the lowest concentration measured using method ISO EN 15192. Today there are no restrictions or guidelines from the environmental authorities in Norway as to which method is accepted or preferred. A study of different analytical methods to determine Cr(VI) in concrete should be conducted in order to allow the most realistic method to be selected.

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