LEACHING BEHAVIOR OF WASTE ZEOLITE AND MUD FROM A ZINC PLATING INDUSTRY IN CEMENT SYSTEM

Damir Barbir, Pero Dabić, Petar Krolo
Faculty of Chemistry and Technology, Teslina 10, 21000 Split
e-mail: dbarbir@ktf-split.hr

ABSTRACT

This work was performed by leaching samples of Portland cement with various additions of waste zeolite and mud according to leaching test EN 12457. Samples were hydrated 28 days at a temperature of 20°C. The success of the stabilisation and solidification was studied by determination of zinc in the solid samples and solutions, after leaching with EDXRF device.

The concentration of zinc ions in solutions and solid samples depends on the addition of waste zeolite and mud and leaching time. According to the European leaching test EN 12457 acceptable shares of waste material are those when the concentration of zinc in the solution does not exceed regulatory limit. The results show that it is possible to use the additions up to 10 % wt..

Keywords: stabilisation/solidification, leaching, waste zeolite, portland cement, EN 12457

INRODUCTION

Metal finishing facilities involve several operations to modify the surface properties of metallic materials: surface preparation, plating and post-treatment processes. Each step demands a rinsing with water, so this leads to high volumes of liquid effluent containing heavy metals, inorganic anions and other pollutants. Wastewater treatment is neccessery step and it usually includes a physico-chemical operation which generates a special sludge which must be managed accordingly by disposal or reuse [1].

Stabilisation/solidification is common practice applied to treatment wastes with heavy metals such as zinc, lead, chromium and copper. In past decades several treatment systems have been used. Cement-based treatment systems show useful application for the immobilization of inorganic heavy metal sludge. Solidification/stabilization of heavy metals in cementitious matrices can transform the sludge in the form of their insoluble hydroxides and silicates, or may absorb it in the cement matrix reducing their water leachability. Cement system is highly alkaline with high adsorption capacity for metals. In addition to this pH effect, there are very strong interactions between cement components and waste ions. The exact mechanisms are not yet well understood but calcium-silicate-hydrate (C-S-H) gel is usually the main source of the adsorption potential because of its high specific surface area and range of adsorption sites [2].

There was an early interest in the chemical reactions of zinc with cement minerals. During hydration zinc is known to react with the cement clinker and to retard setting. During this process the calcium zincate $CaZn_2(OH)_6 \cdot 2H_2O$ is create like intermediate formation. After few days, calcium zincate was no longer detectable. It is obviously that calcium zincate plays an important role in the chemistry of Zn in cement pastes.

Over time, cement paste will be contacted with water or acidic solutions and leaching might cause decomposition of cement paste and remobilization of heavy metals. It is important to understand the leaching behaviour of the pollutants. Leaching tests allow to determine the parameters that control the release of the heavy metals and the amounts that are released. Those tests have been developed with different objectives and they have different applications for environmental purposes [3-6].

In the present study waste zeolite and mud from a zinc plating plant are selected and processed with portland cement CEM I. The final cement composites were characterized using EN 12457 leaching test. The experimental results show that it is possible to stabilize waste zeolite and mud in cement system and it is possible to determine acceptible share of these additions.

EXPERIMENTAL

All the tests carried on using ordinary portland cement with different additions of mixture of waste zeolite and mud from a zinc plating plant with the weight percent of w = 5 - 30 wt. % with the mud content in the mixture w = 20 wt. %.
Industrial portland cement (CEM I) was a commercial product produced by CEMEX Croatia, Kaštel Sućurac. The chemical composition of the Portland cement and natural zeolite are shown in Table 1.

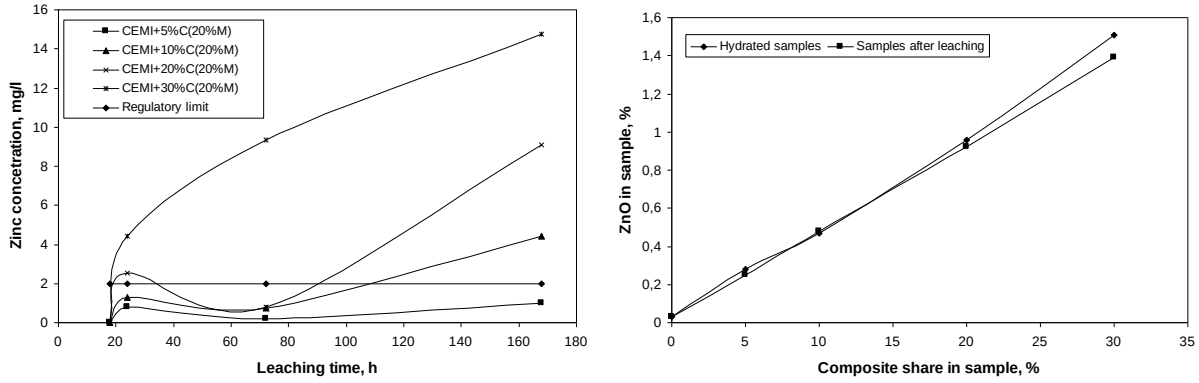
Table 1. Chemical composition of Portland cement and natural zeolite

Chemical composition, (%)	Portland cement	Natural zeolite
SiO_2	22.85	64.93
Al_2O_3	4.81	13.66
Fe_2O_3	2.79	2.03
K_2O	1.79	1.88
Na_2O	0.18	3.66
CaO	65.23	2.99
MgO	1.61	1.10
Loss of ignition		9.84

As the replacement addition to cement it was used natural zeolite which originated from the Donje Jesenje deposits. Zeolite was saturated with zinc ions (saturation with a solution containing 9.0 mmol/dm^3 $ZnSO_4$). Zeolite contained clinoptilolite as the main mineral and impurities such as muscovite, illite, feldspar, sepiolite and quartz.
Mud was obtained from wastewaters of a zinc-plating plant "ADRIACINK" after oxidation (blowing with air) and settling in pools with lime. Mud was gray-brown, small grained and moist. The composition of mud was not constant, and major components were zinc-hydroxide, iron-hydroxide, calcium-hydroxide, and residue from rainfall (soil, sand, dust, detergents etc.).
Waste mud and zeolite were dried at 105°C, ground and sieved through a standard 4900 mesh/cm^2 sieve, so that the size of its particles approximated those of cement.
Samples for the determination of zinc in the eluates were prepared by mixing cement with various additions of mixture of mud and zeolite (5 - 30 % wt.) with the addition of 20 % wt. of mud in the mixture). Samples were hydrated 28 days in a thermostat at a temperature of 20^{o}C. Then samples were inserted in automatic agitator and immersed in distilled water with liquid/solid ratio L/S = 10:1 according to the European leaching test EN 12457. The resulting solutions and solids were tested on the content of zinc after 18, 24, 72 and 168 hours of leaching time.
To determine the concentration of zinc it was used EDXRF device. The concentration of zinc was determined in leaching solutions and the solid samples before and after leaching period.

RESULTS AND DISCUSSION

It is possible to predict possibility of stabilisation of waste mud and zeolite in cement matrix by determination of zinc in solutions and solid samples before and after leaching. Stabilisation process will be successful if zinc concentration does not exceed the limits prescribed by law (2 mg/l). Figures 1. a) and b) show zinc concetration for samples with different additions of mixture mud and zeolite in solutions after leaching and solid samples.



a) b)

Figure 1. Zinc concentration in solutions (a)) and ZnO share in solid samples (b)) for samples with various addition of zeolite and mud

Figure 2. shows pH of solutions in different leaching time for different additions of waste zeolite and mud.

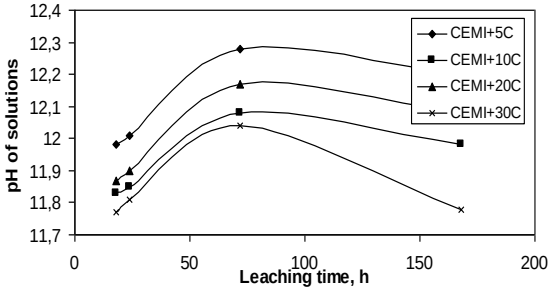


Figure 2. pH of solutions after leaching with different additions of waste zeolite and mud

By increasing the content of mixture (zeolite + mud) the zinc concentration increases in the solutions. According to Croatian law and the leaching test (control point after 24 hours) the results show (Figure 1. a)) that it is possible to use the supplement mixture up to 10 % wt.
In solid samples after leaching it was determined reduced content of zinc, which was expected (Figure 1. b)). pH of solutions increases with longer leaching time but after 72 hours it slowly declines for all kinds of extras. In aqueous systems zinc exhibits an amphoteric behaviour. In the pH range between 8 and 12, ZnO or $Zn(OH)_2$ is stable. In the highly alkaline range, zinc exists as ZnO_2^{2-} in the dissolved form. In cement system zinc is mainly enriched in AFm, AFt and CSH following primary hydration. In AFt Zn^{2+} can be incorporated for calcium. On CSH zinc is sorbed as a hydroxide or carbonate. As direct precipitant, $CaZn_2(OH)_6 \cdot 2\ H_2O$ was observed. Alkali leaching from solid samples increases the pH of the solution until 72 hours of leaching which causes precipitation between 12.0 and 12.3 pH units, which is reflected in the reduction of pH in solutions.

CONCLUSION

This paper describes the leaching behaviour of cement and waste material products. The waste material coming from zinc plating plant. By determination of zinc in solutions and solid samples before and after leaching it is possible to predict possibility of stabilisation of waste mud and zeolite in cement matrix. Stabilisation process will be successful if zinc concentration does not exceed the limits prescribed by Croatian law (2 mg/l). According to law limitation and the leaching test (control point after 24 hours) the results show that it is possible to use the additions up to 10 % wt.. By measuring pH it is possible to follow the processes taking place in the cement system. Decrease of pH in solutions after 72 hours of leaching can be explained by the processes of precipitation between 12 and 12.5 pH units.

REFERENCES

[1] J. Viguri, A. Andres, C. Ruiz, A. Irabien, F. Castro, *Trans IchemE*, 2001, **79**, Part B.

[2] K.Y. Cheng, P. L. Bishop, *Journal of Hazardous Materials*, 1990, **24**, 213-224.

[3] F. Ziegler, C. A. Johnson, *Cement and Concrete Research*, 2001, **31**, 1327-1332.

[4] E. Martens, D. Jacques, T. Van Garven, L. Wang, D. Mallants, Geochemical modeling of leaching of Ca, Mg, Al, and Pb from cementitious waste forms, *Cement and Concrete Research*, 2010, Article in press

[5] J. N. Diet, P. Moszkowicz, D. Sorrentino, *Waste Management*, 1998, **18**, 17-24

[6] C. S. Poon, L. Lam, S. C. Kou, Z. S. Lin, *Costruction and Building Materials*, 1999, **13**, 427-432.