Available online at www.sciencedirect.com
SciVerse ScienceDirect
Procedia Engineering 57 (2013) 1192 – 1197
Procedia Engineering
www.elsevier.com/locate/procedia

11th International Conference on Modern Building Materials, Structures and Techniques, MBMST 2013

# Verification of the Possibility of Solidification Product Made of Neutralization Sludge Use in the Building Industry

BozenaVacenovska[a,*], Vit Cerny[b], Rostislav Drochytka[c], Boris Urbanek[d], Eva Vodickova[e], Jitka Pavlikova[f], VladimirValko[g]

[a,b,c]*Institute of Technology of Building Materials and Components, Faculty of Civil Engineering, Brno University of Technology, Veveri 331/95, 602 00 Brno, Czech Republic*
[d,e]*GEOtest, a.s., Smahova 1244/, 627 00 Brno, Czech Republic*
[f,g]*.A.S.A., spol. s r.o., Dablicka 791/89, 182 00 Praha 8, Czech Republic*

**Abstract**

This paper deals with hazardous waste solidification /stabilisation, specifically neutralization sludge that comes from active industrial sources and neutralization sludge that comes from old ecological sources. As solidification agents fluidized bed combustion ash, classic fly ash and ordinary Portland cement were used. According to the valid legislation and selected possible future use of solidification product a laboratory testing of proposed solidification /stabilisation recipes was performed. The results of leachability tests, unconfined compressive strength and ecotoxicological test showed that solidification product use as a technological and reclamation material on depots and setting pits is possible.


Selection and peer-review under responsibility of the Vilnius Gediminas Technical University

*Keywords*: neutralization sludge; solidification / stabilisation; hazardous waste; reclamation; leachability; landfill.

## 1. Introduction

Neutralization sludge (NS) creates a key group of the industrial waste produced in the Czech Republic both currently and in the past (old ecological loads). NS can be characterized as hazardous waste (HW) originating after the neutralizing of waste acids from various industrial productions which contain hazardous substances. According to the catalogue of waste (Regulation No. 381/2001 Coll.), catalogue number 19 02 05 – Sludge from physical-chemical processing containing hazardous substances – can be uniquely assigned to NS. The issue of old ecological loads (OEL) began to be resolved in the Czech Republic in the 1990s although it still exists today and according to available sources (Ministry of Finance of the Czech Republic website) there are still over 300 localities with unresolved parts or partially resolved OEL. Parts of these localities are loaded with NS depots while other parts require ground work to remove contaminated material and replace with suitable filling material.

The objective of the project which is resolved at the Brno University of Technology, Faculty of Civil Engineering with two representatives of the application sphere is, on the basis of theoretically produced recipes and after verification of their efficiency under laboratory conditions, to develop a new technological line and to also verify the efficiency of these recipes on this newly developed line where NS will be modified into a form enabling it to be used in the reclamation process and in the building industry to fulfil valid legislative requirements. The consequent step will be certification of such prepared products. A key factor influencing the whole process of waste modification will be the economic sustainability of the newly implemented process.

* Corresponding author.
*E-mail address:* vacenovska.b@fce.vutbr.cz


Selection and peer-review under responsibility of the Vilnius Gediminas Technical University
doi:10.1016/j.proeng.2013.04.150

After the accession of the Czech Republic to the European Union, in addition to Government Directive No. 163/2002 Coll., Government Directive No. 190/2002 Coll., is valid which states the technical requirements for CE marked products. According to Government Directive No. 190/2002 Coll., it is necessary to be applied if a harmonized European technical specification exists for the product. Government Directive No. 190/2002 Coll. does not state the list of products; products are classified under this Government Directive once they are harmonized and European technical specifications are issued for them. Then the products are transferred from Government Directive No. 163/2002 Coll. to Government Directive No. 190/2002 Coll.

Only such technical manuals were selected from the existing technical manuals which relate to products which could be suitable inputs to the solidification - stabilisation (S-S) process for NS with the aim of creating a new product by processing the old one.

## 2. Future use of modified waste

*Filling and reclamation material during the resolution of old technological loads*. If an OEL locality is in an industrial zone or a waste depot is directly rehabilitated, there is the possibility to apply the product as filling / reclamation material to the original location under the conditions for complying with the stated rehabilitation limits. These limits in ecologically exposed zones are less strict than limits for the storage/use of material on the surface of the terrain. In this case, the recipient of the product will be a company removing the ecological load and in certain manner also the acquirer – a corporate body on whose land the rehabilitation work is carried out. In reality it is the use of products as technological material in the depots of the company, which participates in the resolution of the project.

*Technological and reclamation material on depots and setting pits.* It is possible to accept waste and materials at depots as technological material which is used for the continuous covering of waste and for safe construction of the depot body in accordance with the project documentation and ensure the stability of the depot and enable to construct temporary access routes in the depot body. The product can be used as technological material, if it:

1. fulfils the parameters for placement in the depot;
2. is approved by the operating rules for the depot;
3. has suitable physical, biological and chemical properties, and
4. is not in a liquid status.

Concerning depots, the product must fulfil the requirements for waste, i.e. for a depot in the order waste category, it must fulfil the IIa leaching class for category S-OO1, IIb leaching class for category S-OO2 (from 1. 4. 2012, S-OO2 depots are considered as the sub-group of S-OO1 depots), for the hazardous waste category depot, it must fulfil the III leaching class. Stabilized (solidified) hazardous waste can be deposited in the depot for the order waste category while keeping to the parameters of the of leaching class for the respective depot category. The content of harmful elements in dry matter is not stated in the stabilized waste.

*Construction material during common ground work.* The application of waste on the surface of the terrain is limited by the fulfilment of the parameters of Regulation No. 294/2005 Coll., Tab. No. 10.1 (dry matter) and 10.2 (ecotoxicity). The content of pollutants in the dry matter is very difficult to estimate from the principle of the origin of the NS which often contains metals and salts from neutralized solution residues, used during surface modifications of metal products and during the processing of waste of various origins in waste water treatment plants. There is non-proportional production of NS from the viewpoint of the stability of their composition. The use of the product should be stated in the construction project documentation. Invariability is important for constructions along with the strict keeping of the parameters of the products, as well as the regular character of deliveries. If the product achieves the parameters for deposits on the surface of the terrain, it can be used as filling material during constructions and rehabilitations. Some of the known undermined areas are in the Ostrava region, North Bohemian and Sokolivo brown coal basins.

## 3. Selection of input raw materials

The choice of suitable NS sources was focused on the actual NS sources and historical sources, coming from OEL.

The first step of the survey was to select possible active sources of NS in the Czech Republic. For this purpose, the database of waste originators was used which was created for BUT, Faculty of Civil Engineering by the Czech Environmental Information Agency (CENIA). According to defined economic, technological and ecological criteria, possible suitable active sources of this sludge were selected. The most appropriate of these active sources appeared to be a sludge arising at industrial waste water demulsification station where predominantly is processed grinding sludge and wastewater from electroplating – sludge A. This waste sludge was subjected to S-S process.

The second group of NS sources is old ecological sources (OEL), which were accumulated in the past in various sludge pits and depots throughout the whole territory of the Czech Republic.

Selected OEL is located in the Pardubice Region and it is one of the high-risk sites to be redeveloped in the near future. Mainly wastes from industrial plants from this region were deposited to the landfill which was closed in 1987. Sludge sample taken from the OEL is designated as sludge B.

For economic reasons, ordinary Portland cement (OPC), fluidized-bed-combustion ash (FBC-A) and classic fly ash taken from individual power plants in the territory of the Czech Republic were selected as S-S agents. The choice of OPC was for several reasons, mainly its common availability and its suitable properties leading to expanded use in the process of toxic waste fixation [1-2]. This primarily concerns inflammability and stability in the environment and particularly that it can be used as the activator for other potential binding materials such as power plant fly ashes. These secondary binders will eventually become an integral part of the cement matrix which will use one type of waste (FBC-A, classic fly ash) to fix other more hazardous wastes [3-4].

## 4. Proposal of solidification-stabilisation recipes

As the main principle for the modification of NS into a form enabling use in the rehabilitation process and in the building industry is the S-S process [5], S-S recipes were proposed so that solidification agents are mixed with the NS in such ratios that that in the solidifying recipe the maximum volume of waste is solidified while keeping the required properties of the product and at the same time, the whole process is as cheap as possible. The proposal for S-S recipes was consequently implemented in relation to the analysis with the transport accessibility of possible localities of solidification product recipients and the availability of the source of input raw materials. The waste content was stated as constant and the volume of S-S agents in recipes after the stated steps remained unchanged. For both wastes four S-S recipes were proposed.

## 5. Laboratory testing

Waste is usually mixed with OPC and additives, which influence in the desired manner the properties of the cement and with a sufficient volume of water for starting the hydrating reactions. The S-S process runs and waste is composed into the structure of the cement. As a rule, the output waste reacts with water and cement forming the metal hydroxides or carbonates, which are usually less soluble than the original compounds in waste [6-8].

The testing methodologies mentioned below, as the basic tests for the primary evaluation of the efficiency of S-S recipes, unconfined compression strength (UCS) test, partial leaching test and ecotoxicologicla tests [9].

*Unconfined compression strength test* was ensured due to the absence of the respective legislation for testing S-S product according to the standard CSN EN 12390-3: Testing of hardened concrete – part 3: Compression test of testing bodies The testing bodies are loaded in the testing press which fulfils EN 12390-4. Maximum loading during the crushing of the body is recorded and the compression strength of the concrete is calculated. In accordance with CSN EN 12390-1: Part 1 - Forms, dimensions and other requirements on testing bodies and forms - were cubes with dimensions (100×100× 100) $mm^3$.

An UCS test was selected as the primary indicator of the S-S process efficiency of the receipt and sufficient mechanical resistance of the S-S product [10]. The final S-S product must report a certain minimum strength, because in the place of use or deposition of the S-S product there will act various mechanical interactions (e.g. loading from other layers), during which the S-S product can be damaged and there can occur possible release of pollutants into the environment. Moreover, it is generally assumed that a higher value of strength in compression also provides better physical barriers when the risk of contaminants extraction into the surrounding environment is decreased. If we take into consideration the selected types of future S-S product use, the minimum commonly used limit for UCS is the value 0.4 $N.mm^{-2}$ for additive granulate for fillings and back-fillings for other constructions. This value will be considered as the limit for the UCS test.

Usually after 28 days of hardening when using cement S-S approximately two thirds of cement are hydrated and then the hydration process continues and after about 1 year about 95-98% of cement is hydrated while the two main hydration products are $Ca(OH)_2$ and C-S-H [3], [11]. For these reasons the compressive strength of S-S products was verified not only after 28 days of maturing, but also after 60 days after S-S product producing.

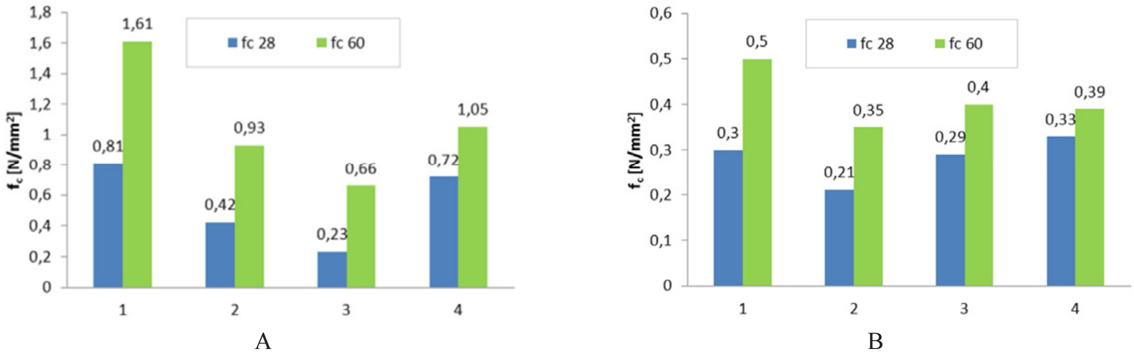


Fig. 1. Graphic evaluation of unconfined compression strength test – sludge A and B

From the measured values of UCS of S-S product of the sludge A (Fig. 1) it is clear that S-S products produced according to recipes 1, 2 and 4 met the limit value for the compressive strength after 28 days of their aging. After 60 days of aging the compressive strength of all S-S products had increased; the highest value of compressive strength was achieved by the recipe 1, in which the fluidized bed combustion ash (FBC-A) with a low content of OPC was used. The recipe 3 did not reach the limit after 28 days aging even if after 60 days of aging there was a significant increase in compressive strength to the value 0.93 $N.mm^{-2}$. This recipe contained except FBC-A and OPC also a classic fly ash. The recipe 4 contained except NS only FBC-A and from the results of these tests it is obvious that the FBC-A worked as a sufficient S-S agent for sludge A.

The values of compressive strength obtained for S-S product made of sludge B show that maximum strength was achieved by recipe 1 as well as by sludge A. In addition to this recipe it met the specified limit of 0.4 $N.mm^{-2}$ after 60 days aging as well as recipe 3. The recipe 2, which contained the highest percentage of classic ash, did not reach a set limit even after 60 days aging. The recipe 4 that contained only FBC-A as the only S-S agent unlike did not demonstrated sufficient compressive strength limit given by the specific applications.

*Leaching test*. An important aspect in terms of usability of S-S product in the building industry is the evaluation of mobility, i.e. extraction of pollutants from the S-S product matrix [12], [13]. The requirements for the waste leaching and leaching class are stated in Regulation No. 294/2005 Coll., including Appendixes. During the preliminary treatment of the S-S product sample and following preparation of a water leachate, the procedure according to CSN EN 12457-4 (83 8005) is applied. The preliminary treatment of sample of waste modified by S-S is contained in Appendix No. 7 of Regulation No. 294/2005 Sb. Technical standards were used for chemical analyses for the analytical determination mentioned in Appendix No. 12 of Regulation No. 294/2005 Coll. As the basic evaluation of the extraction capability on a large number of S-S products was prepared according to basic recipes, the determination of the conductivity of the leachate, pH and the volume of dissolved substances was selected. The conductivity determines the volume of ionising substances in the water leachate – mostly these concerns dissolved inorganic salts. These dissolved salts cause the increase of osmotic pressure and then the leachate reports toxicity caused by the high concentration of these ions (e.g. Na, K, Ca, $Cl^-$, etc.). In terms of conductivity, the maximum Value of 250 $mS.m^{-1}$ corresponds to the 1st leachate class, the maximum value 600 $mS.m^{-1}$ to the 2nd leachate class and the maximum value of 2000 $mS.m^{-1}$ to the 3rd leachate class. At the same time, there is also the relation between the conductivity and the volume of dissolved substances in the leachate. Monitoring of pH values is also important for the reason that it influences the dissolubility of metals, i.e. their extraction capacity from the S-S product matrix.

Table 1. Results of leaching tests – sludge A and B

| Recipe No. | pH | Conductivity [mS/m] | Dissolved solid substances [mg/l] |
|---|---|---|---|
| A1 | 7,34 | 270 | 3314 |
| A2 | 8,00 | 279 | 3570 |
| A3 | 7,96 | 233 | 2830 |
| A4 | 8,06 | 295 | 3764 |

| Recipe No. | pH | Conductivity [mS/m] | Dissolved solid substances [mg/l] |
|---|---|---|---|
| B1 | 12,30 | 1200 | 4074 |
| B2 | 7,34 | 150 | 1594 |
| B3 | 10,53 | 97 | 942 |
| B4 | 7,90 | 118 | 1210 |

In terms of conductivity, respectively according to the content of ionized substances in the water leachate, results of the partial leaching tests (Table 1, 2) showed that S-S products prepared according to recipes 1 to 4 correspond to 2nd leaching class. Only the recipe 1 for sludge B did not complied. It can be said according to the pH value detected by this S-S product that the high pH of the cement based S-S could result into leaching of amphoteric metals (Pb and Zn) [14]. This also indicates the high value of the indicator dissolved solid substances. According to the content of dissolved solid substances in water leachate of S-S products of both wastes S-S products can be classified to the category S-OO1 (2) and can be used as a technological and reclamation material in landfills and sludge beds.

*Ecotoxicological tests*. For selected recipes, on the basis of previous test results, ecotoxicological tests are conducted. These tests enable to simulate the influence of the solidified sludge on the environment. Ecotoxicological tests are biological experiments carried out in order to determine whether a potentially toxic sample, when taken into the environment, causes a biologically significant response in the tested organism. Requirements for the content of pollutants for the use of waste on the surface of the terrain are stated by Regulation No. 294/2005 in Appendix No. 10, which in Table No. 10.2 states the requirements for eco-toxicological tests. Appendix No. 11 defines the conditions for the use of waste on the surface of the terrain where for various methods of the use of waste on the surface of the terrain, requirements are defined for the results of eco-toxicological tests either according to column I or column II mentioned in this appendix. Technical standards for the analytical determination of ecotoxicological tests are mentioned in Appendix No. 12 of Regulation No.294/2005 Coll. Tests are conducted on four types of organisms and are governed by:

- CSN EN ISO 7346-2 – Determination of acute lethal toxicity of pollutant for freshwater fish.
- CSN EN ISO 6341 – Test of inhibition of the mobility of Daphnia magna Straus (Cladocera, Crustacea) – Test of acute toxicity.
- CSN EN ISO 8692 – Test of inhibition of the growth of freshwater green alga.

The methodological instruction of the waste department for the determination of eco-toxicity of waste published in the Bulletin of the Ministry of Environment No. 4/2007, Regulation No. 294/2005 Coll., and Regulation No. 376/2001 Coll. – test of inhibition of the growth of mustard root.

S-S recipes those showed the highest compressive strength for both HW, were subjected to ecotoxicological tests. An aqueous leachate was prepared according to CSN EN 12457-4. The sample was crushed before leaching to a particle size <10 mm. The leachate's pH was adjusted to pH 7.8 ± 0.2 according to Decree No. 294/2005 Coll. Results of leaching tests are shown in Table 2.

Table 2. Results of leaching tests – sludge B

| Parameter | Column I. | Column II. | Results [%] | |
|---|---|---|---|---|
| | | | B | A |
| Inhibition of the mobility of Daphnia magna Straus | max. immobilizat. 30 % | max. immobilizat. 30 % | 70 | 20 |
| Acute lethal toxicity of pollutant for freshwater fish | no mortality | no mortality and behavioural changes | 0 | 20 |
| Inhibition of the growth of freshwater green alga | max. inhibition of growth 30 % | max. changes of growth 30 % | 3,8 | -4,6 |
| inhibition of the growth of mustard root | max. inhibition of growth 30 % | max. changes of growth 30 % | 35,6 | 51,4 |

The results of ecotoxicological tests showed that S-S products failed to meet requirements set by the valid legislation for use on the ground surface and therefore they cannot be used as construction material during common ground works.

## 6. Conclusion

Presented results of S-S of two representatives of NS are just a part of number of different NS that are tested according to the possibility of future use of S-S product in building industry. The results of tests carried out within the scope of this paper showed that the recipes proposed for sludge A (active source of NS) and sludge B (OEL) consisting of FBC-A, classic fly ash and OPC are not suitable for use on a terrain surface. The possibility of S-S product use as a technological and reclamation material on depots and setting pits was verified by partial leaching tests those demonstrated positive results for both NS – in the next laboratory testing the most successful recipes will be subjected to the full-scale leaching tests according to the valid legislation. Favourable results in terms of better mechanical properties demonstrated S-S product made of sludge coming from active industrial source; these S-S products have higher mechanical resistance and therefore the range of its final use has a wider range of options.

Finally after full-scale verification of recipes efficiency under laboratory conditions, they will be tested on a new technological line to also verify the efficiency of these recipes on this newly developed line where NS will be modified into a form enabling it to be used in the reclamation process and the building industry to fulfil valid legislative requirements.

## Acknowledgements

This paper has been developed with the support of project TA01021418 "Technology of neutralization sludge application in the reclamation process and in the building industry"

## References

[1] Asavapisit, S., Naksrichum, S., Harnwajanawong, N., 2005. Strength, leachability and microstructure characteristics of cement-based solidified plating sludge, Cement and Concrete Research 35(6, June), pp. 1042-1049. ISSN 0008-8846.

[2] Sora, N., Pelosato, R., Botta, D., Dotelli, G., 2002. Chemistry and microstructure of cement pastes admixed with organic liquids, Journal of the European Ceramic Society 22(9-10, September), pp. 1463-1473.

[3] Spence, R. D., 2000. Book-Chemistry and microstructure of solidified waste forms, p. 288. ISBN: 0873717481

[4] Chindaprasirt, P., Jaturapitakkul, C., Sinsiri, T., 2007. Effect of fly ash fineness on microstructure of blended cement paste, Construction and Building Materials 21(7, July), pp. 1534-1541. ISSN 0950-0618, 10.1016/j.conbuildmat.2005.12.024.

[5] Spence, R. D., Shi, C., 2005. Stabilization and solidification of hazardous, radioactive and mixed waste. Boca Raton, FL 33431: CRC PRESS. 1-56670-444-8.

[6] Zhang, J., Liu, J., Li, C., Jin, Y., Nie, Y., Li, J., 2009. Comparison of the fixation effects of heavy metals by cement rotary kiln co-processing and cement based solidification/stabilization, Journal of Hazardous Materials 165, pp. 1179-1185.

[7] Stegemann, J. A., Zhou, Q., 2009. Screening tests for assessing treatability of inorganic industrial wastes by stabilisation/solidification with cement, Journal of Hazardous Materials 161(1), pp. 300-306.

[8] Stegemann, J. A., 2004. Chapter 7: Interactions between contaminants and binders, in "Stabilization/Solidification of Hazardous, Radioactive and MixedWastes", R. Spence, C. Shi (Eds.), CRC Press, pp. 151-175.

[9] Pavlitova-Letkova, Z., Urbankova, K., 2010. "Sledování vlastností hmot se zapracovaným odpadem - nové přístupy", Odpadové fórum 2010.

[10] Malviya, R., Chaudhary, R., 2006. Factors affecting hazardous waste solidification/stabilization: A review, J. Hazard. Mater. 137, pp. 267-276.

[11] Park, C.-K., 2000. Hydration and solidification of hazardous wastes containing heavy metals using modified cementitious materials, Cement and Concrete Research 30, pp. 429-435.

[12] Zuberova, J., 2011. Hodnocení výluhových vlastností monolitických odpadů, Odpadové fórum 1/2011. p. 21.

[13] Hills, C. D., 2007. "Introduction to the science behind stabilisation/solidification technology", Stabilisation/ Solidification Symposium, Halifax, Nova Scotia.

[14] Li, X. D., Poon, C. S., Sun, H., Lo, I. M. C., Kirk, D. W., 2001. Heavy metal speciation and leaching behaviours in cement based solidified/stabilized waste materials, J. Hazard. Mater. A 82, pp. 215-230.

[15] Hadj-Sadok, A., Kenai, S., Courard, L., Darimont, A., 2011. Microstructure and durability of mortars modified with medium active blast furnace slag, Construction and Building Materials 25(2), pp. 1018-1025.