Commercially Produced Silicone Polymers as a Possible Binder of Hazardous Wastes

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Summary

Stabilization/solidification is an advanced, environmentally acceptable and commonly used treatment process for hazardous waste before its disposal into a landfill. However, common methods of stabilization/solidification are not sufficient in some cases and therefore some new binders for this purpose are studied. One of the options can be silicone polymers that could replace conventional binders such as cement, fly ash etc. The silicone polymers are hydrophobic, resistant to UV radiation and stable in the environment in a wide range of weather conditions. They are capable to form a hydrophobic barrier on the surface of waste particles and thus prevent leakage of harmful substances into the environment. As a source of the silicone polymer is used commercial product Lukofob ELX (water emulsion of methyl silicone resin). This study is focused on utilizing these properties and verifying the efficiency of the mentioned stabilization/solidification method on chromium contaminated synthetic waste. The properties are verified by three measured parameters: conductivity, pH and concentration of chromium. After that, these parameters are compared with limits set by regulatory decree No. 294/2005 Coll. Two different methods for leaching of stabilized/solidificated waste monoliths are also assessed in this study. One of the methods is carried out by the CSN EN 12457 with solid to liquid ratio 1:10 and the second method is performed by upgraded procedure, where the tested solid is hung on a hook in PVC-coated cage with same ratio solid to liquid. Some ideas are implied at the end of this article, but further analysis will be needed to prove or disprove the capability of commercially produced silicone polymers to stabilize and solidify hazardous wastes with successful results, which are demanded by waste producers.

Keywords: silicone polymers, stabilization, solidification, leaching test

Introduction

Stabilization / solidification (S/S) of hazardous wastes is one of the methods used to prevent environmental pollution and immobilize pollutants (especially heavy metals) in the matrix. After this type of treatment, the waste can be disposed into a landfill or used as a construction material. If the S/S of waste using conventional binders such as cement, fly ash, etc. is not successful, new methods using other binders for waste treatment are studied. One type of those binders could be silicone resins, which are commonly produced and used for example as high-temperature resistant coatings, weather resistant exterior coatings and impregnation of concrete. Silicone polymers are composed of silicon atoms linked by Si-O-Si bonds (polysiloxanes), and the remaining valences are bound to hydrocarbon radicals. The most common types of silicone resins are methyl and or phenyl – substituted polysiloxanes dissolved in an organic solvent, e.g. xylene. Their properties include long-term resistance to weather conditions, especially resistance to UV radiation and temperature fluctuations, hydrophobicity, good chemical and biological resistance [1, 2].

Material and Methods

Testing of the following properties was performed using synthetic waste with the addition of potassium dichromate ($K_2Cr_2O_7$) solution. This addition should assure that the concentration of chromium in the leachate exceeded regulatory limit for leachate class number III, i.e., 7.0 $mg.l^{-1}$ set by decree No. 294/2005 Coll. of the Ministry of the Environment of the Czech Republic [3]. Solidification mixture of the total weight of 240g was prepared from 180 g of silica sand, 60g of cement (II / BS 32.5 R, CEMMAC, Slovak Republic) and 50 ml of solution with concentration of 300 $mg.l^{-1}$ $K_2Cr_2O_7$. This mixture was left for 14 days to harden in cylindrical forms with diameter of 29mm and height of 70 mm.

The tested solids of stabilized/solidified waste were subsequently removed from the form and painted twice by silicone resin coating or acrylic paint. The coatings were left to dry for 2-3 days in the air at ambient conditions. Commercial product Lukofob ELX (Lučební závody a.s., Kolín, Czech Republic) was used as a source of silicone resin. Acrylic paint (ETERNAL, Austis as, Prague, Czech Republic) was used as a reference sample. The effectiveness of the S/S technique used was evaluated in two ways. The first way was a leaching test according to CSN EN 12 457, with the solid to liquid ratio 1:10, using vibrating shaker (RS 10 BASIC YELLOW LINE) at the shaking frequency of 120 rpm for 24 hours (leaching method A) as shown in the Figure 1 [4].

The second leaching method (method B) was also performed at the solid to liquid ratio of 1:10, but the tested solids were put into a cage made from PVC-coated wire netting, which was hung on a hook (see Figure 1). The extraction liquid was stirred by magnetic stirrer at about 300 rpm for 24 hours. This method should leach the tested solids only by liquid flow and thus prevent the disruption of the upper layers of solid and mechanical contact with extraction bottle.

After 24 hours contact time, the leachates were filtered

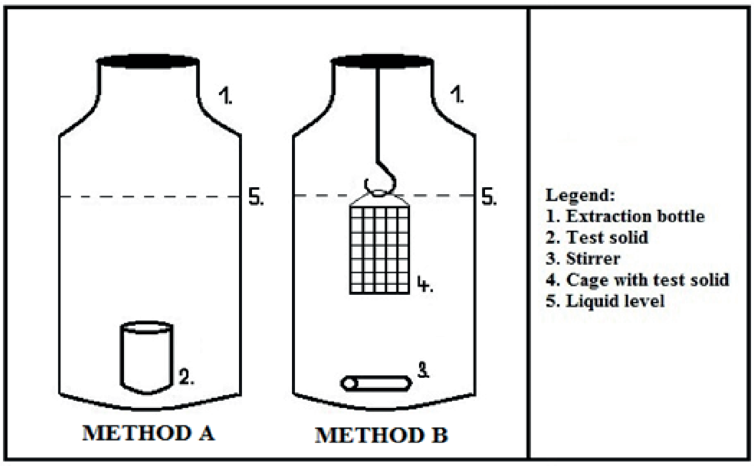

Fig. 1 The scheme of leaching tests

Rys. 1 Schemat procesu ługowania

Tab. 1 Results of leaching tests of stabilized/solidificated waste

Tab. 1 Wyniki ługowania stałych/zestalonych odpadów

Test solid	Extraction method					
	A - Shaking			B - Stirring		
	γ (mS.cm^{-1})	pH (1)	c_{Cr} (mg.l^{-1})	γ (mS.cm^{-1})	pH (1)	c_{Cr} (mg.l^{-1})
WT[a]	2.2	11.8	23.2	2.4	12.3	35.8
PA[a]	0.9	11.2	10.4	0.8	11.3	8.1
LFB[a]	0.1	9.5	1.1	0.1	10.4	0.9

through filter paper (glass microfiber type Z, ø = 50 mm, pore size 5 μm, manufacturer Papirna Pernstejn Ltd.) to separate the solid and liquid phases, after that the filtrate, i. e., the leaching extract, was tested for pH values (pH meter inoLab 730 gel electrode Sentix 41, WTW, Germany), for the chromium concentration in the leachate (atomic absorption spectrometer, GBC 933A , Australia) and for the conductivity (inoLAB cond 730 conductometer, WTW, Germany).

Results and discussion

The results of leaching tests are shown in Figure 2 and in the Table 1. As can be seen from the results, tested solids treated by silicone resin Lukofob ELX met the criteria for leachate class number IIa set by decree No. 294/2005 Coll., whereas specimens coated with acrylic paint did not meet the limit criteria [3]. This suggests that Lukofob ELX has a better ability to form an effective barrier that prevents leaching of chromium than reference sample of acrylic paint. The value of the chromium concentration in the leachate for leaching method A decreased from 23.2 mg.l^{-1} for specimens of stabilized / solidified waste without treatment to 10.9 mg.l^{-1} for specimens painted with acrylic paint, and to 1.1 mg.l^{-1} for specimens treated with a silicone resin.

In the case of leaching method B, blanks of empty cages in distilled water and in alkaline medium (pH = 12) were leached to exclude the contamination of the extracts by chromium from leaching apparatus. The measured values of the blanks were negligible, so the leaching test of the tested solids could be proceeded and the concentration of chromium in the leachate was 35.8 mg.l^{-1} for the specimens of stabilized/solidified waste without treatment. This value decreased to a concentration of 8.1 mg.l^{-1} for the specimens treated with acrylic paint. If the specimens were treated with a silicone resin, the value of the concentration of chromium decreased to 0.9 mg.l^{-1}, which was below the regulatory limit for leachate class number IIa as shown in Figure 2.

As shown in the Table 1, the pH values were measured for both methods and did not exceed the regulatory limit values for leachate class number IIa, i.e., ≥ 6 [3]. The pH of the leachate for stabilized/solidified waste in individual methods ranged from a high of 12.34 in the specimens of stabilized/solidified waste without treatment to the minimum of 9.49 in the case of solids treatment with silicone resin. The next parameter measured to determine the total content of ions in solution and for comparison of different methods and their effectiveness in S/S of waste was specific conductivity. The lowest measured value of conductivity was 0.1 mS.cm^{-1} for tested solids treated with silicone resin in both methods A and B. This indicates, if all measured parameters were compared, that the silicone resin could be used as a binder for successful macro-encapsulation of solidified waste and results of leaching tests are below the regulatory limit for leachate class number IIb, i.e., 1.0mg.l^{-1} set by decree No. 294/2005 Coll. in case of method B [3].

The concentration of chromium in the leachate of un-

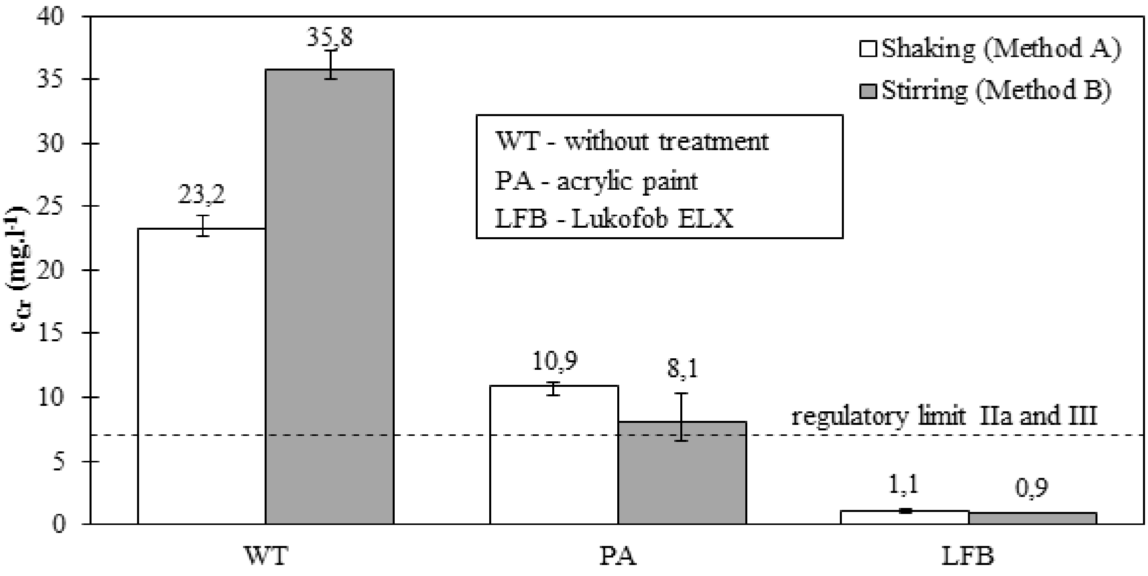

Fig. 2 Concentration of chromium in leachates of solidified waste

Rys. 2 Stężenie chromu w stałych odpadach po ługowaniu

treated specimens produced by method B was higher than in the leachate of untreated specimens produced by extraction method A. That proves that this method is at least as effective as or even more effective than leaching method A. However, leaching of the treated specimens leads to an increase of the chromium concentration in the leachate for leaching method A, because there is a disruption of the top layer and the tested solids can be mechanically damaged on the wall of the extraction bottle, which is undesirable. These data show that leaching method B is more appropriate for solidification, which is the main mechanism of immobilization of pollutants from the coating, i.e., the protective barrier.

Conclusion

- Leaching test B using stirring of the solidificated waste was shown to be as effective as a method A using shaking leaching, while upper layers of solidified waste are not disrupted.
- Efficiency of the barrier depends on the content of the silicone polymer in a solution.
- The concentrations of chromium in leachates of the tested solids coated with a silicone resin were below the regulatory limit for leachate class number IIa.

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Wytwarzane komercyjnie silikonowe polimery jako substancja mogąca wiązać odpady niebezpieczne

Stabilizacja/zestalanie są zaawansowanymi, przyjaznymi dla środowiska i powszechnie stosowanymi sposobami obróbki odpadów niebezpiecznych poprzedzającymi ich składowanie. Jednakże popularne metody stabilizacji/zestalania nie są wystarczające w niektórych przypadkach, a zatem badane są nowe spoiwa do tego celu. Jedną z możliwości mogą być polimery silikonowe, które mogą zastąpić konwencjonalne środki wiążące, takie jak cement, popioły lotne itp. Silikonowe polimery są hydrofobowe, odporne na działanie promieni UV i stabilne w środowisku, w szerokim zakresie warunków pogodowych. Są one zdolne do wytworzenia hydrofobowej bariery na powierzchni cząstek odpadów, a tym samym mogą zapobiec wyciekowi szkodliwych substancji do środowiska. Jako źródło polimeru silikonowego stosuje się produkt komercyjny Lukofob ELX (emulsja wodna metylowej żywicy silikonowej). Praca ta koncentruje się na wykorzystaniu tych właściwości i weryfikacji skuteczności wymienionego sposobu stabilizacji/zestalania z zanieczyszczonych chromem odpadów syntetycznych. Właściwości są weryfikowane przez zmierzenie trzech parametrów: przewodności, pH i stężenia chromu. Następnie parametry te są porównywane z limitami określonych przez dekret wykonawczy nr 294/2005 Coll. Dwa różne sposoby ługowania stabilizowanych/zestalanych odpadów monolitów są również oceniane w tym badaniu. Jedna z metod jest przeprowadzana przez CSN EN 12457 w stosunku 1:10 stanu stałego do ciekłego, zaś druga metoda jest przeprowadzana z użyciem ulepszonej procedury, w której badana substancja stała jest zawieszona na haku, w klatce pokrytej PVC w tym samym stosunku stanu stałego do ciekłego. Pewne idee zostały zasugerowane na końcu tego artykułu, ale konieczne będą dalsze analizy, aby udowodnić lub obalić możliwości produkowania komercyjnie polimerów silikonowych dla potrzeb stabilizacji i zestalania odpadów niebezpiecznych z uzyskaniem wyników, które są wymagane przez producentów odpadów.

Słowa kluczowe: polimery silikonowe, stabilizacja, zestalanie, ługowanie