Journal of Mining and Metallurgy, 42 B (2006) 25 - 31

INVESTIGATION OF POSSIBILITIES FOR HIGH HEAVY METAL CONTENT SLUDGES UTILIZATION BY INCORPORATING THEM IN CONCRETE PRODUCTS

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(Received 21 May 2006, accepted 15 July 2006)

Abstract

The safe removal of sludge, obtained during the surface treatment of different metal products, is a serious environmental problem. These sludges are usually characterized by a high content of heavy metals (Pb, Cu, Ni, Zn, Cr, Cd, Mn), low quality and are obtained in many small industrial units in the whole country, which makes their centralized treatment difficult. In world practice, different methods are used for component fixation of such sludge, in the aim to prevent leaching of the metals causing pollution of the soil and underground water. The aim of the recent work is to prepare the sludge in a form of light (keramzit) fillers by preliminary treatment with binding substances and to introduce them in non supporting concrete products - curbs, stakes and similar products. The investigation was made with two types of sludge - from a production line for thermal treatment and hardening of different parts used in machine-building and from a production line for surface decoration treatment (nickel-plating and chromium-plating) of consumer products. The sludge were dried and ground and then granulated with a solution of water glass. After their solidifying the air dried granules with a size of 5 to 15 mm were treated with cement milk and air dried again. With the obtained granules, standard percolation test for leaching metals like Pb, Cu, Zn, Ni and Cr was carried

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out. After a preliminary calculation of concrete mixtures, these granules were mixed with Portland cement and concrete sample products were made. These molded concrete samples were characterized by their density, water absorption, and mechanical strength for defined standard periods of time. The samples were subjected to a modified percolation test for leaching metals. The metal concentration in eluates was determined by Atomic Spectral Analysis.

Keywords: Stabilization, solidification, heavy metals, hazardous wastes

1. Introduction

In the surface treatment of metals and metal products various in composition and consistence wastes (sludge, precipitate) containing heavy metals are generated sometimes in considerable concentrations. Such treatment is carried out most often in comparatively small enterprises in many places of the country where there are no conditions for centralized collecting of the hazardous wastes and their treatment with the purpose of safe disposal and even less for their utilization. In most cases they gradually accumulate on the area of the enterprises and in some cases they are deposited uncontrollably which results in serious ecological problems.

In compliance with Directive EC 1999/31 of 26 April 1999 of the Council of the European Union even the specialized depots for hazardous wastes, which are not yet built in our country, should receive only wastes subjected to pre-treatment to fix the hazardous components in the waste and reduce to minimum the possibility for their leaching by rain waters [1].

The ideas suggested nowadays for stabilization of the hazardous industrial wastes, some of them applied in the world practice, could be classified in several groups - solidification by addition of cement, solidification by addition of lime, covering the wastes by thermoplastic materials (bitumen, paraffin, polyethylene, etc.), solidification by addition of organic polymers or other binding agents, vitrification of the waste by melting with SiO2. Different combined techniques for fixing are also examined with the purpose to achieve simpler and cheaper treatment [2, 3].

The present paper investigates the possibility for stabilization of high heavy metal content sludge by granulation in advance by means of solution of soluble soda glass (water glass) and utilization of the produced granules as "light filler" in standard concrete mixtures for the manufacture of non critical products [4].

2. Experiments

2.1 Raw materials

For the purposes of the study, we have used sludge from reservoir-neutralizer in a purifying plant after a line for heat treatment of steel parts of the company "M + C Hidravlik", Kazanlak.

The sample obtained from the sludge is characterized by quantitative ICP AES analysis after acid decomposition and conventional chemical methods. Table 1 presents the results.

Table 1. Content of hazardous components in sludge from reservoir-neutralizer in purification plant of the company "M + C Hidravlik", Kazanlak after line for heat treatment of steel parts

Hazardous components	SO_4	PO_4	Ni	Mn	Fe	Cd	Cr	pH
Content mg/kg	806	693	287	456,6	25659	2,8	662,4	10,10

For the purposes of investigation we have also used soluble soda glass of module m = 2,4 and density ρ = 1,45 g/cm^3.

For the surface treatment of the granulated sludge and the preparation of concrete mixtures Portland cement grade CEM (B - M) 32,5 R is used, under BDS EN 197 - 1.

2.2 Method

The bulk density of representative, air dried sample (humidity 0,6%) from the examined sludge is determined and after that the granulation of the required sludge quantity starts. The granulation is performed in disk granulator by using water solution of soluble soda glass as binding reagent. The ratio between the water and soluble glass is 1 : 1. The granulated sludge of maximum granule size 15 mm is spread in a thin layer and dried in air for 24h. The dried granules are sifted through a sieve of 4 mm size of the holes, providing in this way granulometric composition of 4 to about 15 mm, which is suitable for a filler of concrete mixtures [5, 6, 7].

The granules produced in this manner are subjected to surface treatment. The surface treatment of the granules aims to reduce water absorption. It consists in wetting the granules by laitance - 50 g cement and 100 cm^3 water.

The dried granules are immersed in the laitance, drained off and spread again for drying and solidification of the cement coating.

With the granules treated in that manner, in their capacity of "light filler", standard concrete mixtures are prepared and then concrete samples with dimensions 40/40/160 mm are formed of them.

The untreated sludge, granules and concrete samples made of them are subjected to test for the heavy metals extractability (leaching) by percolation test in compliance with Directive EC 1999/31 of 26 April 1999 *(PrEN 14405: Characterisation of waste - Leaching behaviour test - Up-flow percolation test) [1].*

The percolation test ends after collecting the first portion of eluate of about 100 ml at the established infiltration rate of the order of 15-20 ml/h. It undergoes chemical analysis for the components (Ni, Mn, Fe, Cd, Cr) of interest to us. The registration of the final result is directly by the concentration C0 in mg/l (in the first 100 ml of eluate, at ratio "liquid : solid" = 0,1 l/kg). The data obtained are compared with the boundary values of solubility (extractability) of the hazardous components from hazardous wastes that have to be disposed in accordance with the Directive EC 1999/31.

Table 2 shows the results of the leaching tests and particularly the content of the hazardous components in the eluates from the percolation test for extraction, for not stabilized sludge, stabilized sludge (granulated by binding reagent - water solution of soluble soda glass and subsequent surface treatment of the granules by laitance) and concrete samples prepared by incorporating the produced granules, in their capacity of "light fillers", in standard concrete mixture, respectively.

From the results presented in that manner it is seen that all five metals examined for leaching are fixed very well by the used three stage method of treatment.

Extractability of heavy metals from stabilized sludge is many times lower than that of the not stabilized (not treated). In the concrete composition this extractability decreases more and achieves minimum values - < 0,05 mg/dm3.

This is a result of the interaction between the soda glass and the calcium silicates of the cement which leads to formation of calcium hydrosilcates of low solubility additionally hardening the surface layer of the granules and the cement matrix [8, 9].

Table 2. Analytical results for heavy metal content in the percolation test eluate

	Ni		**Mn**		**Fe**		**Cd**		**Cr**		pH
	Norm	Eluate content	Norm	Eluate content	Norm	Eluate content	Norm	Eluate content	Norm	Eluate content	
	mg/dm^3	mg/dm^3	mg/dm^3	mg/dm^3	mg/dm^3	mg/dm^3	mg/dm^3	mg/dm^3	mg/dm^3	mg/dm^3	
Eluate from unstabilized sludge	12	14,31	–	38,02	–	256	1,7	< 0,05	15	21,92	9,34
Eluate from granulated sludge	12	0,17	–	0,05	–	60,6	1,7	< 0,05	15	0,22	10,74
Eluate from concrete blocks	12	< 0,10	–	< 0,02	–	1,7	1,7	< 0,05	15	< 0,05	10,95

For checking the exploitation properties of the granules produced on the base of sludge and applied subsequent surface treatment, they were incorporated in concrete matrix in their capacity of "light filler" [10, 11].

After the preparation of the concrete samples, they are subjected to test of the basic physics-chemical characteristics which they have to meet. Table 3 presents the data.

It is seen in Table 3 that the concrete samples prepared on base incorporation of the stabilized sludge as "light filler" in standard concrete mixtures meet the main standard characteristics for manufacture of non critical concrete products.

3. Conclusions

The experimental results obtained provide the basis for the following conclusions:

1. The investigated sludge of reservoir-neutralizer of purification plant after line for heat treatment of steel parts falls in the list of hazardous wastes because of the high heavy metal content (Ni, Mn, Fe, Cd, Cr).
2. The applied three stage treatment for stabilization of the sludge by granulation with solution of soluble soda glass, surface treatment of the granules by laitance and incorporation of the produced granules in concrete matrix in their capacity of "light filler" shows results that completely meet the European requirements for disposal of hazardous wastes.
3. The concrete samples prepared on the base of incorporating the stabilized sludge as "light filler" in standard concrete mixtures meet the main standard indicators for manufacture of non critical concrete products.
4. An effective method for stabilization and appropriate using of sludge, containing heavy metals, has been established in compliance with Directive EC 1999/31 of April 26 1999.

Table 3. Basic physics-chemical characteristics of concrete samples made on base - incorporation of the granulated sludge in its capacity of "light filler" in standard concrete mixture

Characteristic	Test value	Designed grade of light concrete
1. Volume weight of concrete, kg/m^3		
- in dry condition	1914	1800 - 2200
- in wet condition	2031	
2. Water absorption, %	11,23	-
3. Mechanical strength to pressure, MPa		
- after 7 days	3,25	
- after 14 days	6,56	
- after 28 days	12,82	B 2,5 to B 7,5

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