Waste Cementation – a Simple, Effective and Economical Waste Treatment

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Abstract. All human activities produce wastes. Some of them are hazardous because of the concentration of toxic elements, so that they should not be released without previous treatment. Therefore the main objective on the management of these wastes is to dispose them in such way that the risks remain as low as reasonably possible. Different waste management strategies can be adopted concerning to technological processes, storage time and disposal options. The immobilisation process consists on the conversion of wastes to solid forms that reduces the potential for migration or dispersion of contaminants from the wastes by natural means. The cementation is one of the useful techniques to immobilise radioactive and hazardous wastes using cement as matrix. The relative simplicity of handling, the extensive experience in civil engineering, the availability of raw material, the relative low cost, the compatibility with water and the high density and mechanical strength of cement products are the main advantages for using this material. In addition the process is simple, cheap and efficient. The cemented waste product should have some properties to assure its handling, storage and disposal. In some cases these products can be used if they have characteristics that comply with environmental and specific regulation for use. The present paper illustrates the use of cementation for the treatment of the wastes containing heavy metals, and other contaminants. Good results were obtained and the leaching tests showed that up to 99% of heavy metals remained in the final product, and the released amount is lower than that established by the Brazilian environmental regulation.

KEYWORDS: Cementation, hazardous wastes, radioactive wastes

1. Introduction

A visible fast industrialization in some Brazilian regions and also in other countries, associated with a disorganized demographical expansion, has had as direct consequence considerable production of all kinds of wastes, especially the industrial ones. However a environmentally correct management of the wastes has not presented the same development, contributing affecting negatively the ecosystem due to their inappropriate handling, transportation and release.

All human activities produce wastes. Some of them are classified as hazardous. In accordance to the environmental regulations [1, 2] hazardous wastes are those whose properties are dangerous or potentially harmful to human health or the environment. They can present risk to the public health, provoking or contributing to the increase of the mortality or incidence of illnesses. One of these properties is the presence of contaminants in concentration higher than the permissible limits. The radioactive wastes are included in this group.

Many chemical elements and their compounds, which are commonly used in the industry are toxic and hazardous, among them are the molybdenum, chromium, zinc, mercury, cadmium, lead and some organic compounds. For example the metallic mercury is a lethal pollutant, easily absorbed by the body systems and through the skin; being a cumulative poison, since there is not many ways to release it from the body. It affects the nervous system, and can cause permanently damage to the eyes and many other parts of the body, and also its compounds. Since the transport of the contaminants through the soil, water, and air impose a severe ecological problem, these wastes should not be released without treatment. This treatment can be any process that changes these properties, so that they have a satisfactory form for the disposal or that remove their potential risk [3, 4].

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2. Cementation

The cementation is one of the immobilization/solidification processes that use the cement as matrix. The relative simplicity of handling, the extensive experience in civil engineering, the availability and the relatively low cost of the cement, the compatibility with water, beside the high density and mechanical strength of cement products are the main advantages for using this material. In addition the process is simple, cheap and efficient. As the process occurs at room temperature it does not need additional energy that is currently a big advantage.

The cemented waste product should have some properties to assure its handling, storage and disposal. Important properties are leaching resistance, long-term chemical and mechanical stability and compatibility with the packaging. Low leachability is generally considered one of the most important properties in the evaluation of an immobilized waste form since it represents the first barrier to the release of contaminants to the environment. It is a very efficient process to treat hazardous wastes with high content of toxic metals, due to the high pH reached in the paste, and several multivalent cations are converted in insoluble carbonates and hydroxides, besides to the fact that metallic ions can be also retained in the crystalline structure, which is produced by the cement minerals [4, 5, 6, 7, 8].

The objective is to produce waste forms or waste packages suitable for storage, transportation and disposal. Many countries use cementitious materials (concrete, mortar, etc.) as a containment matrix for immobilization, as well as for engineered structures of disposal facilities. The selection of the conditioning process depends on the waste streams and on the acceptance criteria for the storage or disposal options. These criteria are established to avoid unacceptable release of contaminants to human being and to the environment. This release depends on the physical-chemical properties of the waste forms, waste packages and the environmental conditions.

Many studies have been made to understand the chemical interaction among the cement and the contaminants [9, 10] aiming to increase the range of wastes that can be cemented and to improve the retention capacity of the contaminants, the efficiency of the process (higher waste/cement relation) and the quality of the end product. In summary the main objective is to combine the effectivity of the cementation in retaining the wastes to competitive costs. The water/cement (w/c) and waste/cement (r/c) relations establish the main properties of the waste product, like, porosity, permeability and the temperature gradient due to the hydration. And these ones influence mechanical properties of the end product. The additives are used in case of a poor waste retention or in order to improve the cement-waste compatibility.

Some cemented products that contain other wastes that are not radioactive, could be used if they present characteristics that comply with environmental and specific regulation for use. In this case it should be proved that the contaminants are retained in the product, and then they can be used for example as floor, bricks, reducing the amount of waste to be sent to the landfill, and the environmental impact.

3. Cementation at CDTN

At Centro de Desenvolvimento da Tecnologia Nuclear – CDTN – (Nuclear Technology Development Center) the cementation began with the purpose of solidifying the sludge from the chemical treatment of the liquid wastes generated in the RD&I activities and analyses in the radioactive installations and laboratories. The variety of radioactive wastes generated is as wide as the range of these activities. They include from small volume of solutions to large contaminated pieces.

Since 1979 a research has been developed at Centro de Desenvolvimento da Tecnologia Nuclear (CDTN/ CNEN/Brazil) to find Brazilian natural materials that could be useful in the waste cementation. Clays were investigated more carefully in view of their availability in the whole country, their large industrial use and their reasonable physical and chemical properties to the retention of contaminants. For the intensive study the bentonite was chosen because it presented the best results in the preliminary tests and its retention was good. Bentonite is a clay consisting largely of montmorillonite and characterized by its high absorptive power and active colloidal properties, and it is produced of the change of volcanic ash.The R&D works include the evaluation of natural materials and chemical additives that can improve the physical characteristics of the product cemented, and also its capacity for retention of contaminants. It is also searched mixing processes and equipment to improve the cementation efficiency [11, 12].

Besides of managing the wastes generated at CDTN, some research activities are made to improve the waste treatment systems of Nuclear Power Plant Angra 1, what include the cementation of the bottom of evaporator and ion exchange resins [13]. Some research is also made to solidify contaminated oils from pumps and equipment. The R&DI and routine activities take place in the Cementation Laboratory (LABCIM) and the Cementation Plant (Figure 1).


Figure 1: View of the Cementation Laboratory (LABCIM) and theCementation Plant

LABCIM is equipped for carrying out mixtures of wastes and cement and also for performing tests for the characterization of the wastes, pastes and waste forms, that means for developing and controlling the cementation process and evaluating the waste form quality. To determine the parameters and properties of process and products these mixtures are submitted to the necessary tests like viscosity, setting time, compressive strength and leaching. The Cementation Plant was designed, built and assembled in CDTN using materials of the Brazilian industry, and it is operated in batch, with the capacity of 200 l cemented waste by batch [14]. From the experience gained in the cementation of radioactive wastes [15], work has been developed to treat hazardous waste from industry.

4. Experimental

4.1 Waste

Considerable amounts of wastes are generated by the petroleum industry that are related to exploration, and drilling, which are basically sludge and a mixture of soil, stone and cooling fluid. These wastes are released in pools with other ones coming from all the operations and their volume varies from 16 to 160 m^3 per oil well, which due to the characteristics of the injection fluid have contaminants, especially heavy metals and some organic compound, in concentration above the established limits for discharge without treatment [16]. Some samples from the wastes generated in these operations were studied and characterized to be solidified in cement. The properties and concentration of the contaminants of the wastes are showed in Table 1 and 2, respectively.

Table 1: Some properties of the wastes from petroleum drilling.

Waste	Type	Density (g/mL)	pH	Solid content (%)
FP	Drilling fluid	1.05	9.5	35
FPE	Drilling fluid (Emulsion)	1.01	11.0	86
FPO	Drilling fluid (Oil base)	0.78	8.0	-
C	Sludge with gravel	1.71	10.0	77
BC	Sludge from centrifugation	1.01	11.5	89

Table 2: Concentration (mg/L) of the contaminants in the wastes from petroleum drilling.

Contaminant	FP	FPE	FPO	C	BC
Fe	26,250	879	200	39,300	43,430
Cu	55.6	< 2.0	<2.5	47.7	20.2
Cd	< 4.2	< 3.0	<2.5	<6.8	8.1
Zn	105.0	20.2	7.3	171.0	808.0
Pb	31.5	< 7.0	<7.0	59.8	242.0
Ni	44.1	5.1	<5.0	63.3	12.1
Cr^{+3}	63.0	15.2	<5.3	128.0	30.3
As	< 1	< 1	<1	< 1	< 1
Ba	3,990	5,050	39	38,475	190,890

4.2 Materials

The materials used in the tests are cement, microsilica, bentonite, and cement admixtures.

4.2.1 Cement
Cement Portland with a high initial compressive strength was used.

4.2.1 Microsilica
Microsilica is a byproduct of the silica industry. It is an inert very fine material that is very useful to close the porosity of the solidified product.

4.2.3 Bentonite
Bentonite is a clay whose main component is the montmorilonite, a Hydrate Aluminum Silicate with some quantity of magnesium. It is very efficient for contaminant retention and it has strong sorption and active colloidal proprieties.

4.2.4 Cement admixtures
The cement admixtures are chemical additives used to help the cementation process. Accelerators and fluidizers were tested to improve the mixture characteristics of the cement paste.

4.3 Tests

Many mixtures are studied, and four formulations using different amounts of microsilica, bentonite, and admixtures to improve the workability of the pastes (A, B, C, D) were selected to be evaluated. Tests were performed to determine the main properties of the process and the product. In Figures 2 and 3 are presented some tests for cementation process being performed [11]. In the paste of waste and cement were determined the viscosity, set time and density. Samples of the paste were put in metallic mould, and after 28 days they were evaluated for compressive strength, density, and leachability. The leachability test was performed with monolithic and crushed (pieces smaller than 9.5 mm) samples.

Figure 2 – Tests performed in the paste of cement and waste

Figure 3 – Tests performed in the solidified sample of the cemented waste

4. Results and Discussion

The results from the leaching tests for the different formulations are presented in Table 3 for the monolithic and crushed samples. The concentration of the contaminants in the leachate was so low that it was necessary to develop lower analysis detection limits, and even so the concentrations found were below these values and also below the recommended limits by the standards. In addition both monolithic and crushed samples presented similar results showing that the even the broken waste product can retain the contaminant.

In Table 4 is showed the comparison among the concentration of contaminants in the leachate of the waste “in natura”, the cemented waste product and the standard limits. It can conclude that more than 99% of the contaminants are retained in the cemented product, confirming the efficiency of the process.

In the Figure 4 these results are shown graphically to make easy the comparison among the concentrations of contaminants found in the waste without treatment ("in nature"), the cemented waste product and the values recommended by the environmental regulation. The concentrations of barium and iron found in the waste "in nature" are not plotted, because these values are too high and would difficult the comparison among the other values.

Table 3: Concentration (mg/L) of the contaminants in the leachate from the cemented waste products.

Contaminant	Formulation							
	A		B		C		D	
	M*	F**	M	F	M	F	M	F
As	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Ba	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0
Cd	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pb	<0.4	0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
Cu	<0.05	<0.05	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cr^{+3}	<0.1	<0.1	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
Fe	<0.2	0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Ni	<0.2	0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Zn	<0.05	<0.05	0.1	<0.1	<0.1	0.1	0.5	<0.1

*M = monolithic sample **F = crushed sample

Table 4: Comparison among the concentrations (mg/L) of the contaminants in the waste "in natura", in the leachate from the cemented waste products, and the standard limits.

Waste	**Contaminant (mg/L)**								
	As	Ba	Cd	Pb	Cu	Cr+3	Fe	Ni	Zn
Waste "in natura" (FPE)	<1.0	5,050.0	<3.0	<7.07	<2.0	15.15	879.0	5.05	20.2
Leachate from the cemented waste	<0.5	<3.0	<0.1	<0.4	<0.05	<0.1	<0.2	<0.2	<0.05
Maximal concentration permissible [1. 2]	5.0	100.0	0.5	5.0	250.0	5.0	3.0	0.25	1.8

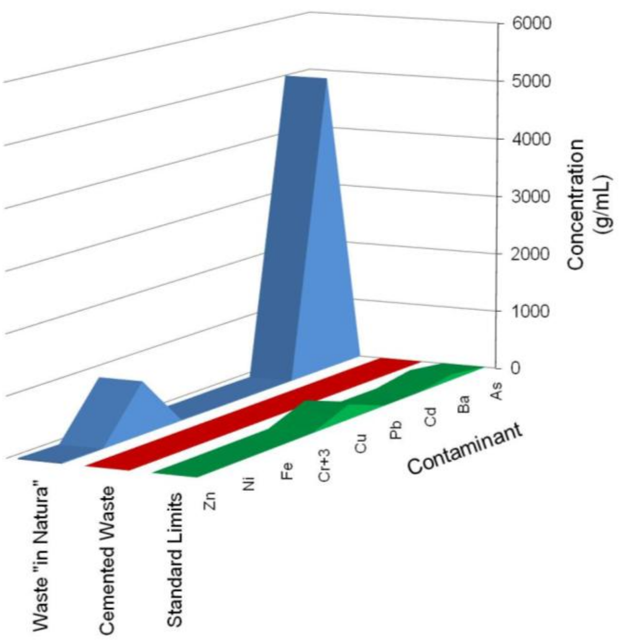

Figure 4: Concentration of the contaminants in waste "in nature", in the cemented product, and the recommended limits by the environmental regulation

To cement these wastes in real scale it is not required large investments in equipment or materials. The most important is to define, first, the destination of the cemented waste, if reuse, such as pavement, or if release in a landfill or storage within a package. From this definition some additional studies are needed to suit the characteristics specific to each destination.

5. Conclusion

The release of hazardous wastes without treatment impacts seriously the environment if the concentration of contaminants is high, because the geochemical transportation of these materials to the aquifers, and to the food chain provides a huge problem of contamination. Then an efficient option to treat them it is always necessary.

The possibility of their solidification with cement has been widely studied around the world with very positive results. The main advantages of this treatment are: the low cost of materials and equipment, the easy operationalization of the process and the final characteristics of the solidified product, which can also be reused without risks.

The results of the compressive strength tests are important for the transport, storage and / or use of the product solidified, but for the environment the leaching tests are more important because they are used to simulate conditions that the solidified waste can be submitted, for example rains, floods and other attack of liquid solutions, which can remove the contaminants from it and lead them to the environment [1, 17].

In CDTN R&D works have been performed in the cementation area looking for materials, processes and equipment that provide solidified products with good quality and can be transported and stored without risk to human being or the environment.

This technology was used for the treatment of wastes from oil drilling containing high concentrations of heavy metals. Mixtures are prepared using additives and different quantities of wastes and cement.The results prove the efficiency of treatment, since more than 99% of contaminants are retained in the product, even when reduced in size and submitted to acid leaching.

REFERENCES

[1] ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS, Resíduos Sólidos, NBR 10004, ABNT, Rio de Janeiro (1987).

[2] BRASIL. CONAMA, Resolução n° 06, de 15 de junho de 1988, Diário Oficial [da República Federativa do Brasil], Brasília: p.92-94, 2 jan. 1989. Seção I, (1989).

[3] POJASEK, R. B., Solid-Waste Disposal: Solidification, Chemical Engineering, v.86, n.17, p.141-145, (1979).

[4] SERIE DE ATAS DA CETESB, Resíduos Sólidos Industriais, CETESB, São Paulo:, n.1 (1985).

[5] McWHINNEY, H. G., COCKE, D. L., A Surface Study of the Chemistry of Zinc, Cadmium, and Mercury in Portland Cement, Waste Management, v.13, p.117-123 (1993).

[6] KINDNESS, A. et al., Immobilization and Fixation of Molybdenum (VI) by Portland Cement, Waste Management, v.14, n.2, p.97-102, (1994).

[7] KINDNESS, A. et al., Immobilization of Chromium in Cement Matrices, Waste Management, v.14, n.1, p.3-11, (1994).

[8] CHEESEMAN, C.R. et al., Heavy Metal Leaching from Hydroxide, Sulphide and Silicate Stabilised/Solidified Wastes, Waste Management, v.13, n.8, p.545-552, (1993).

[9] LI, X. D. et al., Heavy Metal Speciation and Leaching Behaviors in Cement Based Solidified/Stabilized Waste Materials, Journal of Hazardous Materials, v.82, p.215–230, (2001).

[10] RICHET, C. et al., Synthèse des Connaissances sur le Comportement à Long Terme des Bétons Applications aux Colis Cementés, CEA-R-6050, CEA/SACLAY, Gif-sur-Yvette (2004).

[11] TELLO, C. C. O. Avaliação de Bentonitas Nacionais como Aditivo na Cimentação de Rejeitos Radioativos, CDTN-620, MSc Thesis, Univ. Federal de Minas Gerais, Belo Horizonte (1989).

[12] TELLO, C. C. O., “Pesquisa de Aditivos Químicos para a Utilização na Cimentação de Rejeitos Radioativos”, Congresso Geral de Energia Nuclear, 5., (Proc. Cong. Rio de Janeiro, 1994), v.1, p.319-324, (1994).
[13] TELLO, C. C. O.; BARROSO, A. C. O. “Design and Process Improvements on the Waste Treatment of Angra I and Angra II Power Plants in Brazil”, Tenth International Conference on Nuclear Engineering-ICONE10, (Proc. Conf, Arlington, 2002), v.1, (2002).
[14] GABRIEL, J. L., Instalação de Tratamento de Rejeitos de Baixo Nível do CDTN (Filtração/Cimentação), NT-DETQ.PD-001/84, NUCLEBRÁS/CDTN, Belo Horizonte, (1984).
[15] TELLO, C. C. O.; BARBOSA, L. M. V.,” Cimentação: Opção para Tratamento e Remediação”, ICTR 2004 Congresso Brasileiro de Ciência e Tecnologia em Resíduos e Desenvolvimento Sustentável, (Proc. Cong. Florianópolis - SC. 2004) (2004), (CD-ROM).
[16] SEABRA, P. et al., As Atividades de Perfuração e Produção de Petróleo e o Meio Ambiente, Boletim Técnico da PETROBRÁS, v.27, n.1, p.42-49, (1984).
[17] ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS, Lixiviação de Resíduos, NBR 10005, ABNT, Rio de Janeiro, (1987).