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Impact of hardening conditions on to stabilized/solidified products of cement–sewage sludge–jarosite/alunite

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Abstract

The main objective of this work is to investigate a viable alternative for the final disposal of sewage sludge from urban wastewater treatment plants using a mixture with cement and jarosite/alunite (J/A) precipitate to develop new construction materials. J/A precipitate is a waste product of a new hydrometallurgical process, which was developed in order to treat economically low-grade nickel oxide ores. In the current study two methods were used for the hardening of the stabilized/solidified products: (1) in laboratory conditions and (2) in accelerated conditions (autoclave treatment).

For this purpose, mortar prism samples of $4 \times 4 \times 16$ cm in dimension were prepared, composed of 50% sewage sludge, 30% cement and 20% jarosite/alunite. The samples were treated in an autoclave for 3 h at a temperature of 200 °C and a pressure of 16 bar as well as in laboratory conditions for 28 and 90 days. Compressive and bending strength, while chemical, XRD, thermal analysis, as well as tests of leaching, were tested according to the standard/principal methods of toxicity characteristics leaching procedure (TCLP) and CEN/TS 14405. The results indicated that stabilized/solidified products can be produced for use in construction and that the heavy metals of sludge can be contained in the cement and jarosite/alunite mixture.

Keywords: Sewage sludge; Cement; Jarosite/alunite; Stabilization/solidification; Heavy metals; Autoclave

1. Introduction

Stabilization/solidification (S/S) is a widely accepted treatment process for the immobilization of hazardous substances, like heavy metals contained in wastes. It entails mixing these materials with binders and reagents in order to reduce the leaching of contaminants. The most commonly used medium in the S/S process is Portland cement. One of the main objectives of this work is to present an effective alternative for the final disposal of sewage sludge produced by urban wastewater treatment plants by using it as a mortar component. In this study the possibilities of using Portland cement with a waste product of a new hydrometallurgical process, jarosite/alunite precipitate, as binders, and the development of a construction material containing this waste were considered [1]. In the current study two methods were used for hardening of the stabilized/solidified products: (1) in normal conditions and (2) in accelerated conditions (autoclave).

Autoclave treatment of jarosite with sewage sludge yields a product which contains minerals, which are much more stable than the minerals in the original jarosite. Most of the metals are transformed to oxides or even sulfides, which are not leached by the simulated rainwater [2].

Jarosite/alunite (J/A) is a by-product of a new integrated hydrometallurgical method, developed by the Laboratory of Metallurgy of the National Technical University of Athens under which the low-grade nickel oxide ores can be treated in an efficient and economical way. It involves heap leaching of the ore by dilute sulphuric acid at ambient

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temperature, purification of the leaching liquors and recovery of nickel and cobalt. Iron, aluminum and chromium are then precipitated as crystalline, easily filterable salts of the jarosite/alunite type, at atmospheric pressure [3].

The idea of replacing part of the Portland cement used as a binder with this jarosite/alunite precipitate seems rather challenging, considering that the general trend is to develop alternative ways for the recycling of industrial wastes or by-products in order to eliminate the cost of disposal and to avoid soil and water contamination. Several methods for producing new construction materials using different mixtures of industrial wastes, in particular jarosite waste have already been patented [4,5].

The simple use of a binder for the S/S process can make it difficult to determine whether true stabilization has taken place. For this reason a minimum compressive strength of 350 kPa at 28 days is recommended. It is also suggested that in order to determine whether the above process is successful, the leaching tests should give a leachate with a pH value between 7 and 9. Furthermore, the concentrations of the heavy metals in this leachate should be lower than the limit values set by the European Council decision 2003/33/EC for the acceptance of a waste in an inert landfill [6].

2. Experimental

The main objective of this work is to investigate an alternative use for the final disposal of sewage sludge from urban wastewater treatment plants, using mixtures of sewage sludge–cement, to develop new construction materials.

2.1. Type of sludge

The sewage sludge used is a mixture of primary and secondary sludge from the Metamorphosis Wastewater Treatment Plant, in Athens.

Table 1
Sludge characteristics

Parameters	Metamorphosis sludge
Moisture (%)	78
TOC (%)	10
pH	7.00
Heavy metals (mg/g)[a]	
Cr	0.470
Cu	0.460
Fe	13.160
Ni	0.230
Pb	1.090
Zn	2.400

[a] Concentration of heavy metals (mg/g dry sludge).

2.1.1. Sludge characteristics

The sludge was dried and its moisture content and pH were measured according to the standard methods [7]. TOC content was determined by a titrimetric method [8] and its concentrations in heavy metals were measured by means of atomic-absorption spectrometry (Perkin–Elmer 3300) [9]. The results of the analyses are shown in Table 1.

It is evident from Table 1 that the pH was fairly constant at a neutral value of 7.00. This value is expected because the sludge is subjected to neutralization prior to its disposal.

2.1.2. Grain size distribution

Particle size distribution was measured by a laser scattering particle size distributer analyser (CILAS). The result concerning grain size distribution and passing percentages of the Metamorphosis sludge is displayed in Fig. 2.

2.2. Jarosite/alunite precipitate

Chemical analysis of jarosite/alunite precipitate was done by classical wet methods and mineralogical analysis was done by XRD. The results are presented in Table 2 and Fig. 1, respectively.

2.2.1. Grain size distribution

Particle size distribution was measured by a laser scattering particle size distributer analyser (CILAS). The results are shown in Fig. 2.

It is seen that the J/A precipitate appears to be finer, with the cumulative percentage passing at 32 μm being 100% (the corresponding percentage for the sludge is 64.7%) (Fig. 2.).

2.3. Type of cement

Specimens were prepared using Portland cement type CEM II 32.5 and sand according to EN 196-1.

2.4. Sample preparation

Sludge samples in wet conditions were mixed with a binder (cement or cement with jarosite/alunite precipitate), sand and water. The mixing procedure was the same for all pastes. Compressive strength was tested according to the methods described by European Standard EN 196-1 [10]. The composition of mortars prepared (which was calculated according to previous works [11]) is given in Table 3.

Table 2
Chemical analysis of the jarosite/alunite precipitate

Oxides	SiO_2	Al_2O_3	Fe_2O_3	MgO	MnO	LOI	SO_3	Cr_2O_3	CoO	SUM
Concentration (%)	1.20	18.55	39.66	0.46	0.04	20.00	17.34	1.36	0.05	98.66

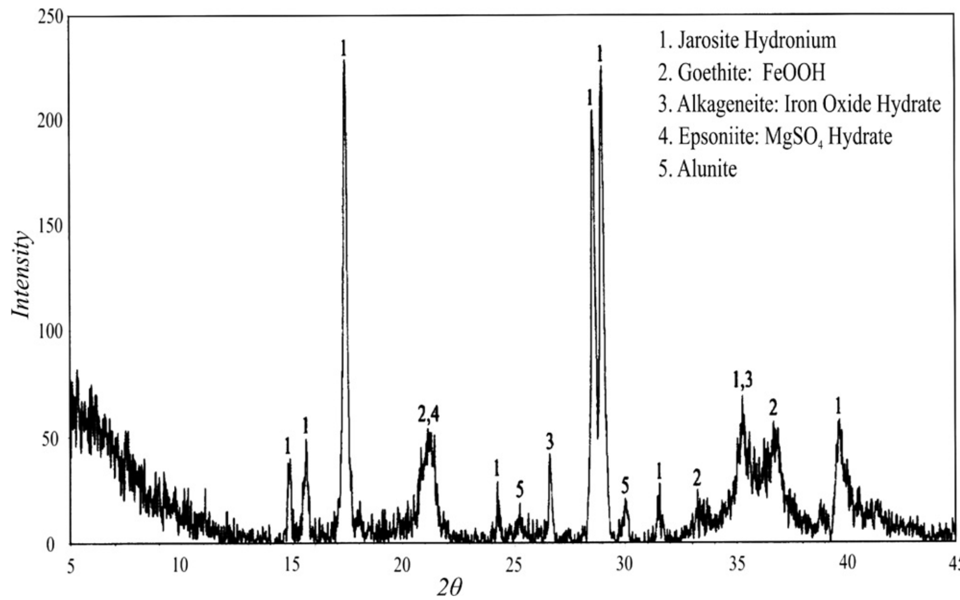

Fig. 1. Mineralogical phases of J/A precipitate.

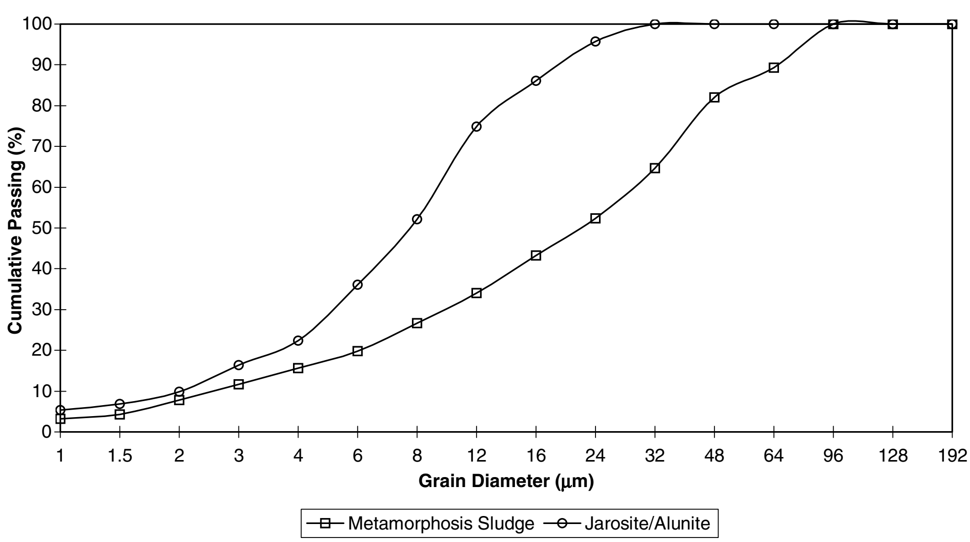

Fig. 2. Grain size distribution of metamorphosis sludge and J/A precipitate.

Table 3
Composition of the mortars

Mortar	Sludge/binder	Sludge solids/binder	Sludge solids/cement	Dry sludge (g)	Cement (g)	Jarosite/alunite (g)	Sand (g)	Water (ml)
MWC	1/1	0.22/1	0.22/1	49.5	225	0	1350	180
MWCJ	1/1	0.22/1	0.36/1	49.5	135	90	1350	185
MWCA	1/1	0.22/1	0.22/1	49.5	225	0	1350	170
MWCJA	1/1	0.22/1	0.36/1	49.5	135	90	1350	180

M: Metamorphosis, W: wet sludge, J: jarosite/alunite precipitate, A: autoclave, C: cement.

2.5. Autoclave treatment

Autoclave consists of a high-pressure steam vessel, equipped with an automatic pressure control and a safety valve.

Two specimens were treated in autoclave in order to accelerate strength development through hydrothermal reactions taking place under these conditions. The other two specimens were jarosite free – cement and cement with jarosite/alunite precipitate. They were treated in the autoclave for 3 h at 200 °C temperature and pressure of 16 bar [12].

3. Results and discussion

3.1. Compressive and bending strength results

The results of the compressive strength tests of the autoclave, 28 and 90 days samples are shown in Table 4.

From Table 4, the following conclusions can be drawn: (A) All of the mixtures exceed the minimum limit of 350 kPa of compressive strength at 28 days; (B) When part of the cement is replaced with the jarosite/alunite precipitate (MWJC and MWJCA) lower values of compressive strength are observed. This fact is compensated by the economic profit because of the use of less quantity of cement.

3.2. XRD analysis results

The formation of C–S–H occurs which, along with ettringite, are responsible for the high compressive strength. The presence of jarosite/alunite favors the formation of ettringite because of the excess of SO_3. The XRD analysis performed confirms the existence of ettringite in all four samples. The XRD diagrams obtained for samples MWJC and MWJCA (both containing J/A) are given in Figs. 3 and 4.

3.3. Thermal analysis methods

The samples were analysed by thermogravimetry (TG–DTA–SDTA). The results are shown in Figs. 5 and 6.

Similar to the DTA and SDTA of Portland cement, here also the chemical interaction takes place which can be divided into:

- Up to 100 °C: removal of water from hydrated products.
- Up to 300 °C: different stages of C–S–H and C–A–H dehydration.
- The endo-peak at 450 °C is due to the dehydroxylation of $Ca(OH)_2$ formed from cement hydration.
- The endo-peak at 750 °C is due to the decarbonation of calcium carbonate, which is a cement component.

Table 4
Compressive and bending strength tests results

Mortar	Bending strength (MPa) (28 days)	Compressive strength (MPa) (28 days)	Bending Strength (MPa) (3 months)	Compressive Strength (MPa) (3 months)	Autoclave	
					Bending Strength (MPa)	Compressive Strength (MPa)
MWJCA	–	–	–	–	0.675	2.125
MWCA	–	–	–	–	1.525	5.140
MWJC	1.120	2.640	1.846	4.365	–	–
MWC	1.450	4.815	2.200	6.500	–	–

M: Metamorphosis, W: wet sludge, J: jarosite/alunite precipitate, A: autoclave, C: cement.

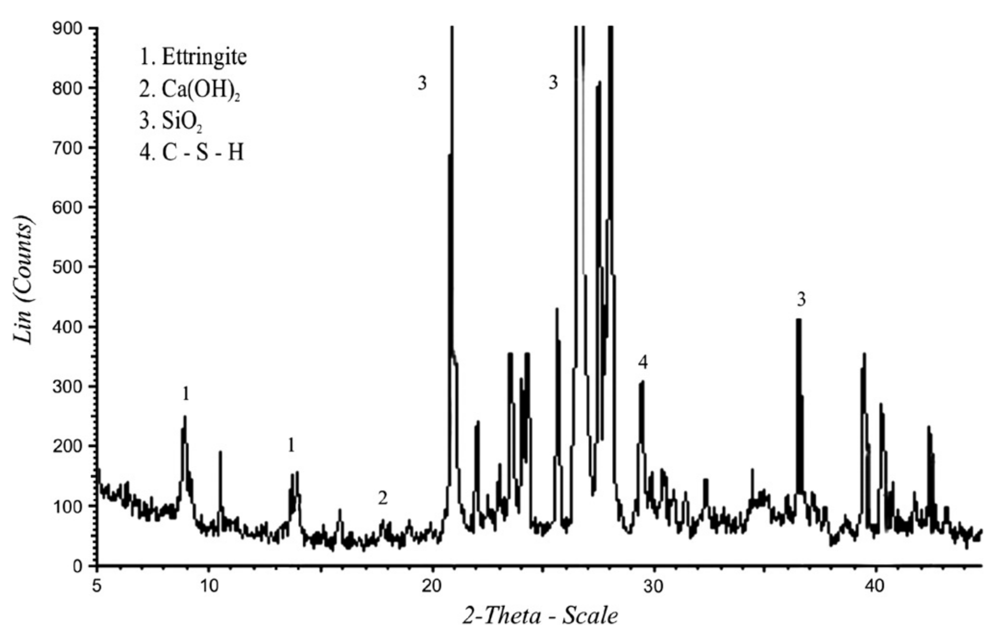

Fig. 3. XRD sample of sludge, cement, J/A (28 days).

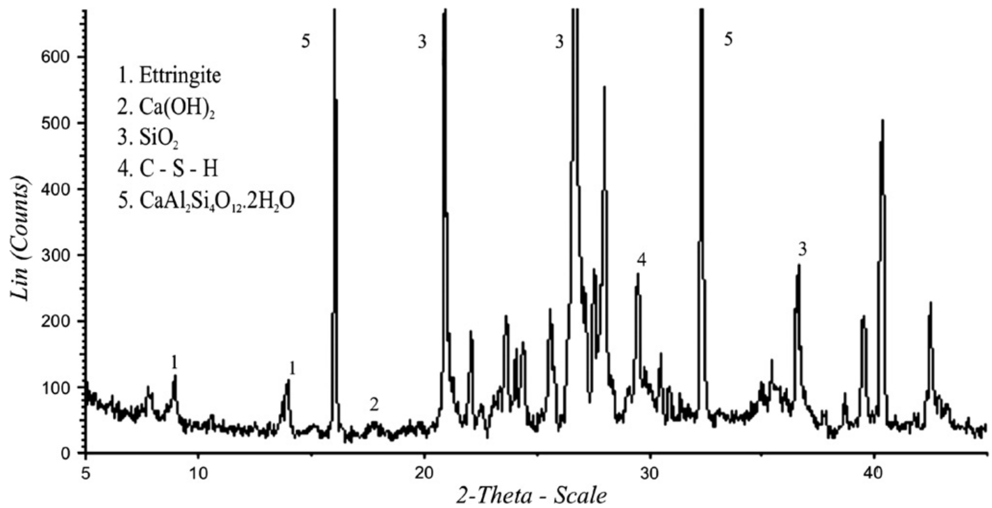

Fig. 4. XRD sample of sludge, cement, J/A (autoclave).

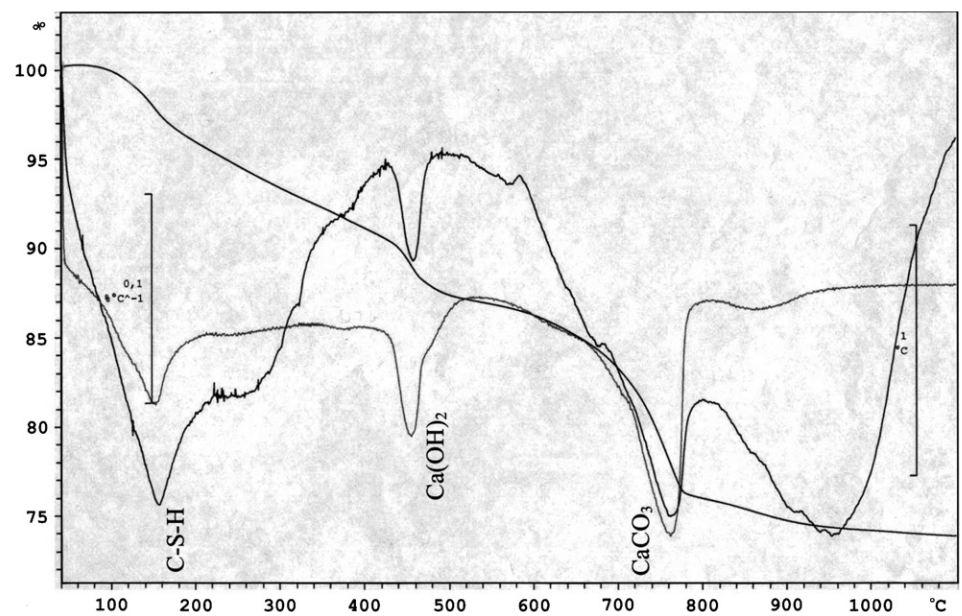

Fig. 5. TG–DTA–SDTA curves of sample MWJC (28 days).

3.4. Leaching tests

The results of the leaching tests are presented in Tables 5a and 5b. The TCLP tests and CEN/TS 14405 tests in order to determine the amount of heavy metals that can be extracted from the samples [6] were carried out for all the samples, since they met the limiting compressive strength which of 350 kPa [13]. Leaching tests were also performed on the original sludges in order to estimate the percentage of metals retained by the binders in the mortar.

- The TCLP and CEN/TS 14405 tests have shown high retention percentages of heavy metals in the cement phases.
- This retention of heavy metal molecules in the hydrated Portland cement appears to be a combination of more than one process.
- It is suggested that some of those are ionic adsorption to the hydrated C–S–H in the hydrated cement paste, ionic incorporation into the crystalline network of some compounds of the hydrated cement such as sulphates in the ettringite hydrate and, finally, physical retention in the porous structure. More investigation needs to be done in this field.
- The use of jarosite/alunite precipitate did not seem to have any effect on metal retention. Thus it appears that the metals are bonded by the cement.
- It is observed from the results of the TCLP and CEN/TS 14405 tests that the retention of heavy metals was found to be of the same order of magnitude for all four samples (both with and without J/A). The autoclave method does not seem to have a strong effect on the retention of heavy metals by the samples.

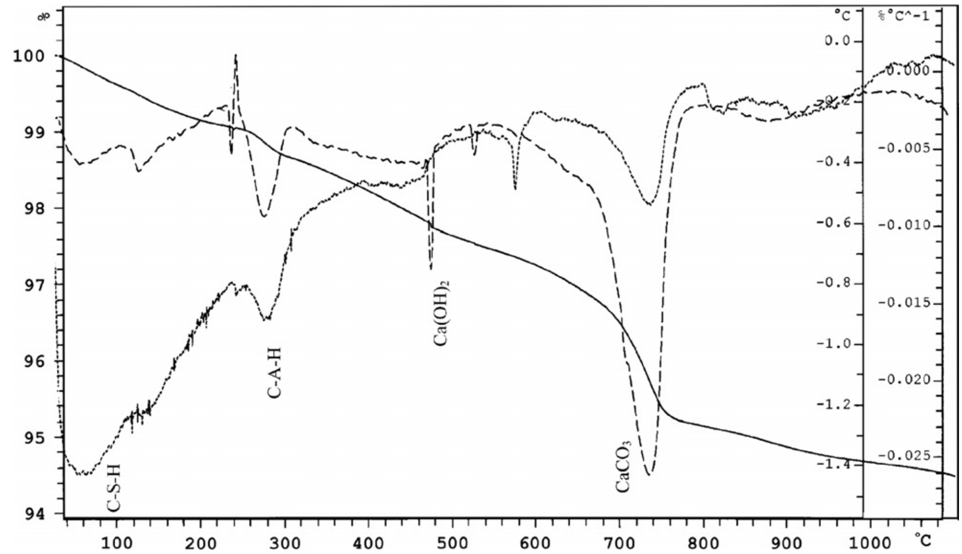

Fig. 6. TG–DTA–SDTA curves of sample MWJCA (autoclave).

Table 5a
TCLP test results and heavy metal retention percentage for metamorphosis sludge

	Cu, ppm	%	Fe, ppm	%	Zn, ppm	%	Ni, ppm	%	Cr, ppm	%	Pb, ppm	%	pH
M	2.43	0	9.40	0	4.20	0	2.22	0	0.73	0	0.30	0	
MWC	0.214	91.2	0.328	96.5	0.015	99.6	0.072	96.7	0.030	95.9	0	100	6.74
MWJC	0.134	94.4	5.298	43.6	0.430	89.8	1.955	11.9	0.142	80.5	0.29	3.33	6.67
MWCA	0.212	91.3	0.548	94.2	0.022	99.5	0	100	0.005	99.3	0	100	6.75
MWJCA	0.590	75.7	1.088	88.4	0.209	95.0	1.841	17.1	0.289	60.4	0	100	6.95

Table 5b
CEN/TS 14405 test results and heavy metal retention percentage for metamorphosis sludge

	Cu, ppm	%	Fe, ppm	%	Zn, ppm	%	Ni, ppm	%	Cr, ppm	%	Pb, ppm	%	pH
M	2.43	0	9.40	0	4.20	0	2.22	0	0.73	0	0.30	0	
MWC	0.179	92.6	0.035	99.6	0	100	0.135	93.9	0.087	88.1	0.22	26.7	6.71
MWJC	0.148	93.9	0.043	99.5	0	100	1.649	25.7	0.109	85.1	0	100	6.75
MWCA	0.185	92.4	0.043	99.5	0	100	0	100	0.009	98.8	0	100	6.71
MWJCA	0.231	90.5	0.093	99.0	0	100	1.250	43.7	0.009	98.8	0	100	6.74

M: Metamorphosis, W: wet sludge, J: jarosite/alunite precipitate, A: autoclave, C: cement.

4. Conclusions

The following conclusions can be drawn from this investigation:

1. Sewage sludge from wastewater treatment plants can be solidified and stabilized in a matrix of Portland cement or Portland cement – jarosite/alunite precipitate by using both methods: (1) in laboratory and (2) in accelerated conditions (autoclave treatment).
2. The TCLP and CEN/TS 14405 tests have shown high retention percentages of heavy metals in the cement phases. This retention of heavy metal molecules in the hydrated Portland cement appears to be a combination of more than one process.
3. The retention of heavy metals by both samples (with and without J/A) is of a similar magnitude. This fact favors the use of J/A precipitate, which is a waste material, since it provides a cost-effective and economical method for treating wastewater sludge.
4. The ultimate goal of this study is the reuse of both waste materials (wastewater sludge and J/A precipitate) into construction materials. From the first results of this investigation, this goal seems to be achievable. However, the final results from the long term and durability experiments – which have been programmed – could give the definite answer to this question.
5. The retention of heavy metals is similar for the samples manufactured under laboratory conditions and for those produced by an autoclave. This fact suggests that

the autoclave method can safely be used to produce samples for studying the retention of heavy metals, without affecting the results. This possibility offers an important advantage by means of the time required for sample preparation.

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