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Studies of Galvanizing Industry Sludge Embedment Possibilities into Concrete Mixtures

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Abstract: Solid residues from the galvanizing industry, called galvanizing sludges, having a high heavy metal content, pH = 9-10 and relative humidity of about 70,82 %. These sludges are toxic, and cannot be deposited beside the urban wastes, and so, there are various possibilities studied for their reprocessing as useful materials: electrochemical recovery, filling materials, etc. In the paper there were some possibilities studied, in order to embed the galvanizing sludges, from S.C. Westmetal S.R.L., in construction materials like: bricks, pavements, concrete plates, etc. The composition of each concrete mixture was studied using Bruker D8 Advance X-Ray Diffractometer). The metal's bonding degree was analyzed during several days, by immersing the samples (shaped like cubes) into water, simulating this way their exposure to repeated, torrential rain. Periodically, the metals concentrations was determined using a novAA 400 G atomic absorption spectrophotometer, equipped with MP60 autosampler, specialized software, WinAAS, for continuous data processing.

Keywords: sludge, wastes, concrete, diffractometer, spectrophotometer.

1. Introduction

At the present time, at national level, the galvanizing industry is producing growing quantities of residues. These residues have high heavy metal content and are produced in form of a slurry paste, with relatively high water or humidity content and they are called sludge's. Not to make a comparison with wastewater treatment sludge's, these ones are highly toxic, due to the heavy metal content. In some cases the even electrochemical recovery was applied, in order to reuse the useful components (metals). Deposition of the above mentioned materials, regardless of their concentration in heavy metals, cannot be done at garbage dumps, beside urban wastes. Special precautions must be taken, to avoid contamination of water and soil.

2. Experimental data

One of the possibilities is to embed them into inert materials, to stabilize the toxic content. Studies regarding the process of sludge embedment into concrete mixtures have been made; some of the most relevant results are presented in the followings.

The concrete, as embedment material, was chosen due to the stabile bonds created after its solidification, and, not to mention the quantities that are being used worldwide at the present day, for various applications, as construction materials.

Different mixtures were prepared, consisting of cement, sand and water and growing quantities of sludge were added. Beside the blank sample, concrete mixture with no sludge and two other samples, containing weighted quantities of sludge.

The general composition for the blank sample, m = 2,340 kg

All three samples weight about the same; because a much larger block/cube of sample would influence negatively the results and other variables, due to weight/surface ratios.

TABEL 1. General composition of blank sample

Components	Quantity, kg
cement	8,2
sand (0-3 mm)	21,4
sand (3-7 mm)	14,2
sludge	-
water	3,5
special aditive	41

The first sample, or "Sample 1" (sludge quantity = 5% of the cement quantity) m = 2,270 kg

TABLE 2. General composition of first/sludge1 sample.

Components	Quantity, kg
cement	8,2
sand (0-3 mm)	21,4
sand (3-7 mm)	14,2
sludge	0,4
water	3,36
special aditive	41

The second sample or "Sample 2" (sludge quantity = 10% of the cement quantity) m = 2,205 kg

TABLE 3. General composition of second/sludge 2 sample.

Components	Quantity, kg
cement	8,2
sand (0-3 mm)	21,4
sand (3-7 mm)	14,2
sludge	0,82
water	3,1
special aditive	41

Generally, the following metals are present in all of the sludge samples, used in the concrete mixtures: Cr, Cu, Zn, Fe, Al; and they were analyzed afterwards.

The concrete-sludge mixtures, poured in cube like shapes, are immersed in ultrapure water, in order to simulate torrential rainfalls. It is very important that the water in which the cubes are immersed to be ultrapure, otherwise the results could be easily influenced, not to mention, pH values, could influence the solubility of some metals.

Conditions, for preparing the samples were identical, identical mixing times, identical type of cement and sand. All of them were kept in the same room, so the temperature fluctuation not to have an effect.

After hardening, one of the most important properties of the concrete cubes was analyzed, their resistance, tested with a special tool, which measures the exact force, needed to crack or break them. The other important feature of the concrete mixtures was the heavy metal content, present in the water, in which the samples were immersed. It was very important for all the variables (pH, temperature, and salinity/conductivity) to be the same for all the samples.

The analyses were made using a NOV-AA 400G, Atomic Absorption Spectrophotometer, year of production: 2006. The following metals were analyzed: Cr, Cu, Zn, Fe, Al. The results are presented as tables and their variations are represented as diagrams.

3. Results and discussions

3. 1. Determination of chromium

TABLE 4. Determination of chromium.

Nr.	Sample	1	5	9	12	15
1.	Blank	40,14	42,34	31,85	28,81	37,18
2.	1	111,3	92,67	66,19	48,90	73,29
3.	2	70,02	40,69	24,28	30,52	50,98

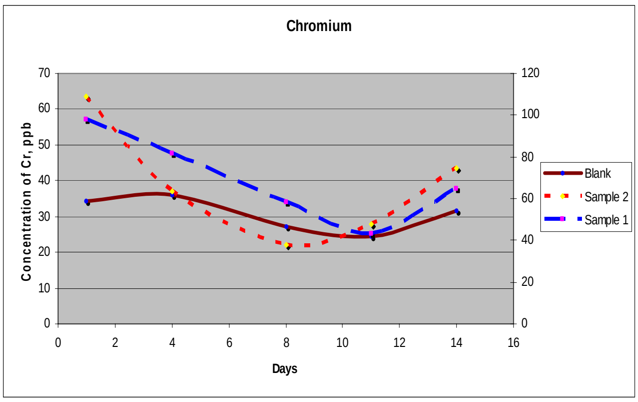

Figure 1. Determination of chromium.

As seen from the representation, figure 1, the values for the 3 samples, (blank, sample/sludge 1 and sample/sludge 2), have a similar allure, the differences are not significant.

3.2. Determination of copper.

TABLE 5. Determination of copper.

Nr.	Sample	1	5	9	12	15
1.	Blank	14,22	13,2	4,775	6,913	4,348
2.	1	23,45	19,88	9,475	15,65	12,17
3.	2	25,05	21,43	7,422	12,44	9,52

Representing the values from the table 5, the variation of copper concentrations, looks like:

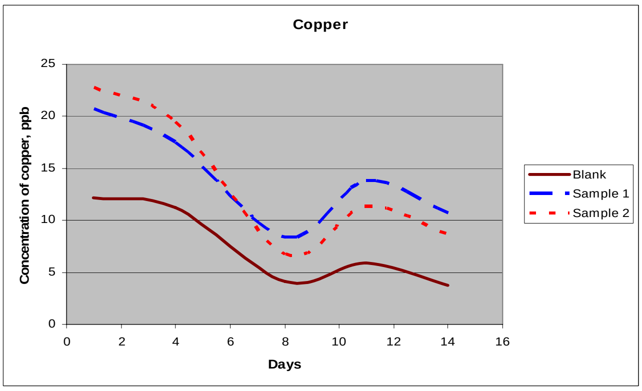

Figure 2. Determination of copper.

The values represented have also a similar tendency to decrease at the beginning and then to slightly increase. No exact interpretation was found, from the studied literature entries. The only logical explanation could be the pH values variation; thus influencing the copper ions stability/solubility.

3. 3. Determination of zinc

TABLE 6. Determination of zinc.

Nr.	Sample	1	5	9	12	15
1.	Blank	2,730	6,225	11,06	na	8,011
2.	1	3,736	na	na	96,7	2,971
3.	2	11,53	6,114	6,453	36,14	8,804

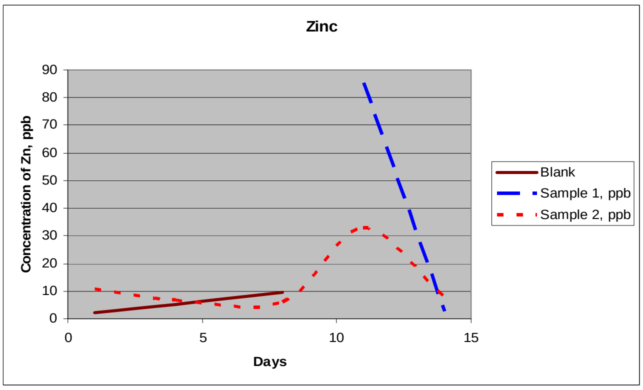

Figure 3. Determination of zinc.

The dramatic decrease of the zinc ions in the second sample is due to technical error of analyses process. As seen from table I.3., the second and third sets of analyses were cancelled, the values being out of range. The other two samples (blank and sample 2) maintain the same tendency with slight differences.

3. 4. Determination of iron.

TABLE 7. Determination of iron.

Nr.	Sample	1	5	9	12	15
1.	Blank	131,9	25,91	216,8	1519	560,7
2.	1	106,5	56,60	136,2	1505	532,9
3.	2	347,3	75,44	165,4	1530	822,9

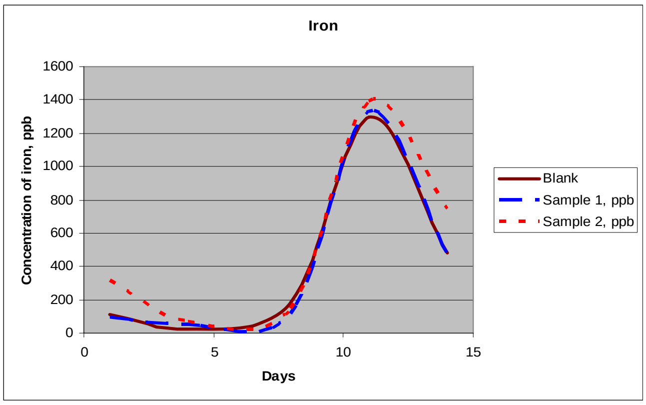

Figure 4. Determination of iron.

The 3 curves, seen in figure 4, tend to have the same allure, from beginning till end. As recorded during analyses processes, there were no other influences. Although having the same increase than decrease tendency, the sudden change in the concentrations can be attributed only to variation of pH values, during the immersion of cubes.

3.5. Determination of aluminium.

TABLE 8. Determination of aluminium.

Nr.	Sample	1	5	9	12	15
1.	Blank	na	89,89	424,9	608,8	413,9
2.	1	na	324,7	225,6	637,9	443,2
3.	2	na	82,74	141,5	552,7	414,6

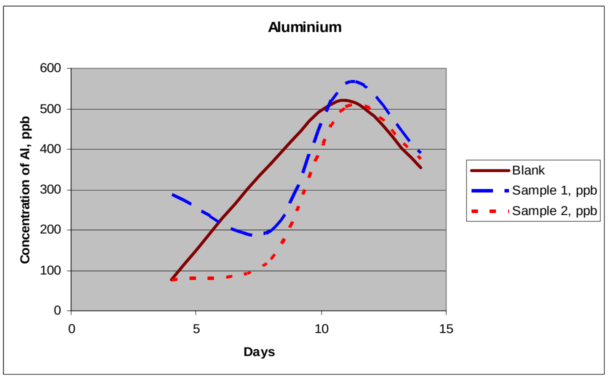

Figure 5. Determination of aluminium.

Similar to the behavior of iron ions, a sudden change (increase and then decrease) around the same time can be observed also in case of aluminium.

3. 6. Variation of pH values.

TABLE 9. Variation of pH values.

Nr.	Sample	1	5	9	12	15
1.	Blank	12,07	11,97	11,95	11,74	11,78
2.	1	11,9	12,03	12,15	11,98	12
3.	2	12,2	12,11	11,72	12,05	12,1

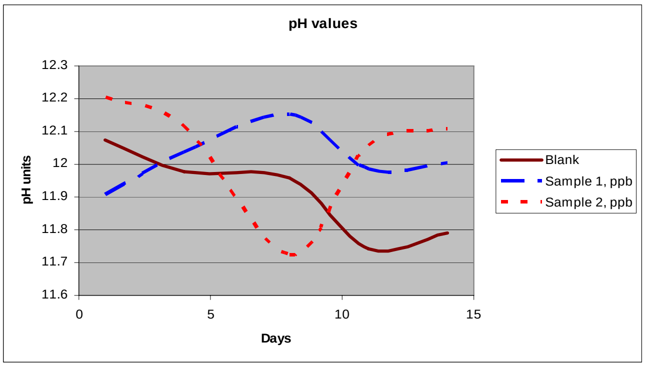

Figure 6. Variation of pH values.

The fluctuations of pH values, as represented in figure 6 does not automatically explain the behavior of metals analyzed and presented above.
Being one of the most important parameter, the pH values were measured simultaneously with 2 apparatuses, the values represented are the mean values between the 2 measurements. It can be stated, that there were no difference greater the 0,1 units between the 2 measurements.

3. 7. Compression tests

Being used as construction material, as mentioned in the abstract too, bricks, pavements, concrete plates, etc., one of the most important properties are the resistance to compression and the apparent density. If these two properties, as values are too low, the resulted material in too weak, not corresponding not even for filling material. In the same time, if the compression resistance test values and apparent density values are too low, directly the hydraulic bounds are too weak, and the metallic ions could be released mare easily.

Their variations are presented in the following tables, the measurement units are N/mm^2.

TABLE 10. Compression resistance test values.

Time [days]	Blank	Sample 1	Sample 2
7	30.4	21.5	20.4
14	34.1	24.8	22.3
28	38.2	30	26.3

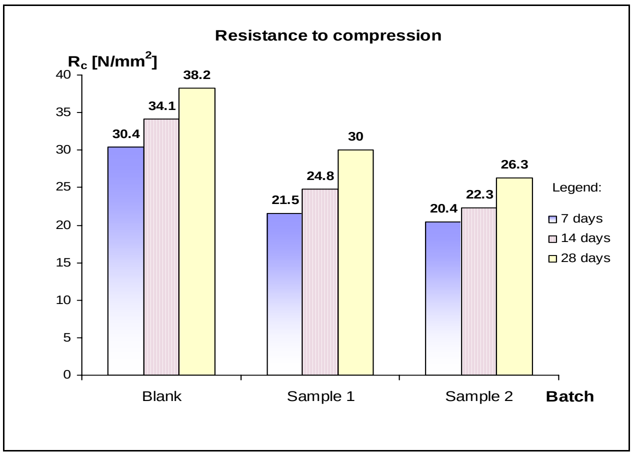

Figure 7. Compression resistance test values and their variations in time.

3. 8. Apparent density tests

Values recorded during the test are as follows:

TABLE 11. Apparent density test values

Time [days]	Blank	Sample 1	Sample 2
7	2343	2236	2260
14	2335	2220	2250
28	2310	2200	2230

Measurement units: kg/m^3
Values are represented in the following figure.

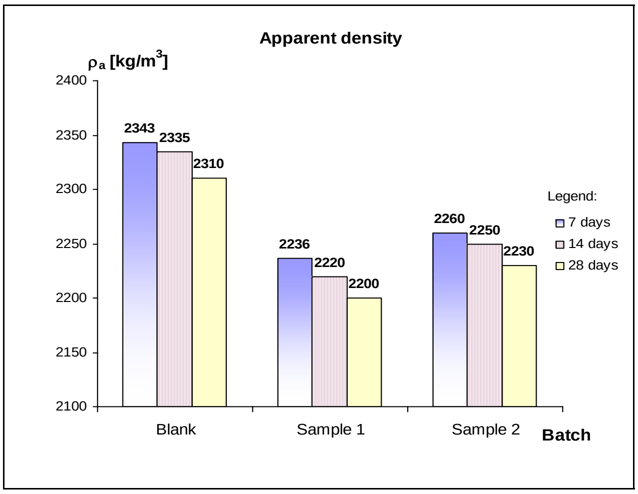

Figure 8. Apparent density test values and their variations in time.

3.9. X-ray analysis

All elements have a characteristic x-ray spectrum produced from their activity, and there is a very strong correlation between atomic number and the frequency of certain lines in the x-ray spectrum; thus the x-ray spectrum can be used to identify elements in a specific sample.
The elements are identified by comparison.

Results of the Bruker D8 Advance X-Ray Diffractometer analyses are X-ray spectra. There was also an X-ray spectra made for the sludge and for (concrete) sample 2 (with higher sludge content). Spectras are presented in figure 9 and fig 10.

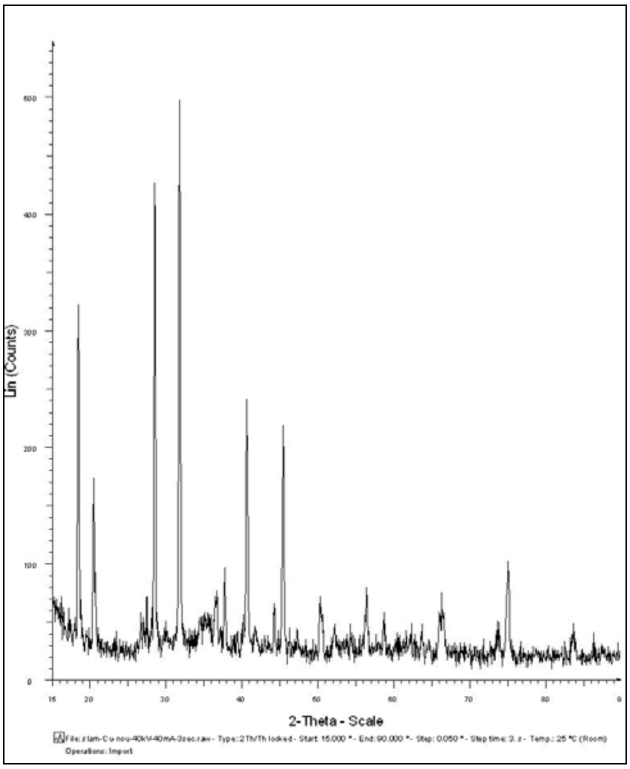

Figure 9. X-ray spectrum for sludge with heavy metal content.

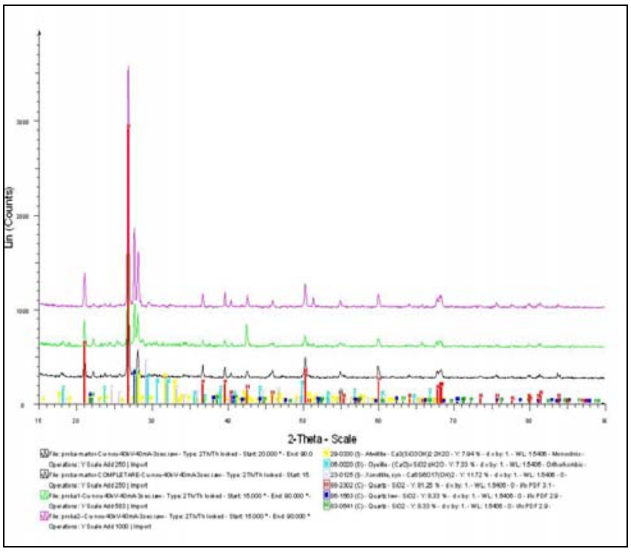

Figure 10. X-ray spectra for concrete with sludge content.

4. Conclusions

The conclusions are a continuity of comments and discussions after each representation, at each subchapter. Each metal's behavior was commented after each representation. Beside a minor technical error, in case of zinc, there were no other factors that could influence, negatively, the results.

Analyzing the obtained data, variation of concentrations for determined metals and the x-ray spectrums, gives us a complete view, regarding the concrete's behavior in actual applications. Of course, the sludge embedment in concrete mixtures, in not a final solution, but could be an alternative for reducing their toxicity, although it would be recommended to use the concretes away from houses, playgrounds, sidewalks, residential areas. However it would be a great filling material for waste dumps, waste pounds, and other applications already in contact with contaminated matter.

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