

Study of the heavy metal content of cement and the possibility of reducing their concentrations in cement dust emitted from cement manufacturing plants in the city of Mosul

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Abstract:

In this research, sixteen samples of dust deposits are collected indoors and outdoors at the two Badoush Cement Factory Expansion and the New Badoush Cement Factory in Mosul city. The aim of the research is identification and estimate the concentrations of the heavy metals in the dust samples emitted from the two Factories and the possibility of reducing the concentration of these metals using an X-ray fluorescence (XRF) device and atomic absorption spectrophotometer. The results of XRF showed the presence of Titanium, Iron, Nickel, Vanadium, Zinc, Chromium, Zirconium, Ruthenium, Europium, Mercury, Strontium, and Aluminum. Other elements appeared in some samples: Gold, Lead, Palladium, Rubidium, and Rhenium. Lead, Iron, Nickel, and Zinc were detected in the dust; Iron showed a higher content level in all samples; it changed between $72.52 \,\mu$ g/ml in sample 6 to $37.59 \,\mu$ g/ml in sample 1 as a minimum level. Nickel ranged between $1.025 \,\mu$ g/ml in sample 1 to $2.875 \,\mu$ g/ml in sample 5. The highest zinc content was detected in sample 16, 0.7555 μ g/ml. Cobalt and cadmium were not detected in all samples.

Keywords: heavy metal, cement, manufacturing, Mosul.

Introduction

Cement is a very soft material. It is an adhesive that has cohesive properties in the presence of water and can bind the components of concrete to each other that sets, hardens, and adheres to other materials to bind them together. Cement is seldom used on its own but rather to bind sand and gravel (aggregate) together. Cement mixed with fine aggregate produces mortar for masonry, or sand and gravel_produce concrete (1, 2). Concrete is the most widely used material and is behind only water as the planet's most-consumed resource (3). Cement is overwhelmingly made by burning fossil fuels like coal and petcock in cement kilns- akin to large furnaces—to heat limestone (raw material) to very high temperatures (~2,640°F/1,500°C). The heat induces a

chemical reaction that transforms the limestone into clinker (1), The gypsum and clinker are then ground together with gypsum to form cement. Emissions from fuel burning are responsible for ~40% of the lifecycle CO_2 emissions in cement (often called embodied emissions) (4). the hydration mechanism is pivotal in developing cements with specific final chemical compositions. Cement dust is one of the most polluting powders released at every stage of raw material extraction, crushing, and manufacturing (5). The content of heavy metals in cement depends on the origin and the composition of the raw materials used. The high-temperature calcination process of limestone and clay minerals can release gases and dust rich in heavy metals into the atmosphere (6). The most common method for the determination of heavy metals is atomic absorption (7). According to the decomposition rate of minerals, heavy metals accelerate the hydration of tricalcium silicate (C3S) and Portland cement. However, they retard the precipitation of portlandite due to the reduction of pH resulting from hydrolyses of heavy metal ions (8). The chemical mechanism relevant to the accelerating effect of heavy metals is H+ attacks on cement phases and the precipitation of calcium heavy metal double hydroxides, which consume calcium ions and then promote the decomposition of C3S (9). The phenomenon of dust is one of the global weather phenomena that causes damage to humans, animals, plants, the natural environment, and the economy because it has not caused any area from the waves of dust that infiltrate everything and cover the touches and the radiation of the respiratory aspects with pollution and its dire consequences on the ground and the style of cities that are not prepared anything to face this danger that is the strongest and facing the earth (10). Cement manufacturing stages through which dust is released is shown in the figure below:



Figure 1. Cement manufacturing stages



Figure 2. Badoush Cement Factory

Experimental material and methods

- Ammonium chloride (BDH), Hydrochloric acid (37%) (Pharmpur), Lead nitrate Pb (NO₃)₂ (BDH), Hydrolyzed zinc acetate Zn (CH₃COO)₂.4H₂O (ANALAR), Ferric chloride FeCl₃ (BDH), Aqueous nickel sulphate NiSO₄ .6H₂O (POCH), Aqueous cadmium nitrate Cd (NO₃)₂.4H₂O (BDH), Aqueous cobalt chloride CoCl₂ .6H₂O (Fluka AG), nomination paper (F2040-150) and Deionized water (provided from Intravenous solutions laboratory).
- Heater (Hot plate-JX-1010B-Turkey), Sand bath (MATEST-Italian), water bath (MATEST-Italian), X-Ray diffraction device (PANalytical-MiniPal4), Atomic absorption spectrophotometer (novAA350-analyitkjena-Germany), Conductivity meter (Xylem Analytics Germany GmbH/Cond3110) and Mortar (Manual).

Collection of the samples

Sixteen samples of dust deposits were collected indoors and outdoors at the two Badoush Cement Factory Expansion and the New Badoush Cement Factory; each sample was placed in clean, dry plastic boxes, marked with the location from which it was taken; the total number of samples reached (16) sample. The samples are then dried in a drying oven, ground using a mortar(mill), and then sieved using a molecular sieve (0.8), This is to prepare it for the required tests of the digestion process, as well as for measurement with an X- ray machine.

Table 1. the collected samples.

Sample	Position	GPS (axis)
1	Filling the silo from its centre.	36.44001,42.93150
2	Silo wall	36.44027,42.93159
3	*Cyclone dust	36.44212,42.93075
4	Shared between mill and packer	36.44020,42.93316
5	Shared between the mill and the packing silo	36.44003,42.93343
6	From under the eucalyptus tree ,100 meters	36.44470,42.93038
	away	
7	Material grinder	36.44432,42.93005
8	**Cooler starter dust	36.44121,42.93061
9	Shared between the mill and packer at a	36.43923,42.93257
	distance 100 meters	
10	From the beginning of the laboratory gate	36.43852,42.92938
11	From the material grinder near the weeds	36.44444,42.93026
12	Shared between the mill and packer at a	36.44042,42.93205
	distance 65 feet north	
13	Shared between the mill and packer at a	36.44571,42.93098
	distance 200 meters	
14	Shared between Expansion silo and New silo	36.43952,42.93340
15	Packing mill at a distance 10 feet north	36.43994,42.93278
16	Shared between packing and silo south of the	36.44001,42.93446
	factory	

*Cyclone: Separating gases from dust grains.

**Cooler:The clinker cools after leaving the kilns.

Sample digestion method:

The samples were digested by taking 1 gram of each sample, mixing with 1 gram of ammonium chloride with a glass stirrer in a 25 ml beaker, then adding 10 ml of concentrated hydrochloric acid, placing the resulting mixture into a sand bath at a temperature between 70 to 80° C with stirring for 40 minutes, then it filtered using F2040 – 150 filter paper and washed by hot water, the filtrated solution diluted to make 500 ml in a volumetric flask.

1- Qualitative analysis

The models were analyzed qualitatively using a device (X-ray fluorescence spectroscopy) (XRF) operated depending on the list of device standards; the results were listed in Tables 2 to 17 for each model, expressed as a percentage.

Mg %	Al%	Si%	S%	К%	Ca%	Ti%	V%	Cr%	Mn%
0.56	1.33	0.47	1.2 6	1.2 9	82.92	0.377	0.032	0.037	0.06 3
Fe%	Cu%	Zn%	Sr%	Zr%	Ba%	Eu%	Yb%	Hg%	Ru%
4.14	0.06 1	0.017	1.1 6	0.0 51	0.24	0.04	0.03	0.016	0
Pd %	Ni%	Re%	Au %	Pb %	Rb%	As%	Os%	Ag%	Υ%
0	0	0	0	0	0	0	0	0	0

Table 2. Elemental content of Sample 1.

 Table 3. Elemental content of Sample 2.

Mg	Al%	Si%	S%	K%	Ca%	Ti%	V%	Cr%	Mn%
%									
1.4	4.43	18.5	0.48	2.97	48.03	1.62	0.095	0.214	0.32
			3						2
Fe%	Cu%	Zn%	Sr%	Zr%	Ru%	Eu%	Pd%	Hg%	Ni%
19.4	0.11	0.034	0.53	0.11	0.916	0.17	0.27	0.03	0.09
6	7		3						4
Re%	Au%	Pb%	Rb	Ba%	As%	Os%	Ag%	Yb%	Y%
			%						
0.06	0.05	0.061	0.04	0	0	0	0	0	0
	5		2						

 Table 4. elemental content of Sample 3.

Mg	Al%	Si%	S%	К%	Ca%	Ti%	V%	Cr%	Mn
%									%
0.9	2.59	11.0	0.7	1.5	70.7	0.82	0.04	0.09	0.15
1			30	9	0	8	9	5	
Fe%	Cu%	Zn%	Sr%	Zr%	Ru%	Pd%	Yb%	Hg%	Ni%
8.9	0.08	0.046	0.7	0.0	0.64	0	0.03	0.02	0
81	8		91	73	6		9	3	
Ва	Ag%	Pb%	Rb	Eu	Au%	As%	Os%	Re%	Y%
%			%	%					
0.3	0.16	0	0.0	0.1	0	0	0	0	0
8			18	1					

Mg	Al%	Si%	S%	K%	Ca%	Ti%	V%	Cr%	Mn
%									%
0.5	1.13	5.79	1.8	2.0	82.1	0.29	0.05	0.05	0.06
5			4	3	2		1	5	0
Fe%	Cu%	Zn%	Sr%	Zr%	Ru%	Eu%	Ba%	Hg%	Ni%
3.5	0.05	0.013	1.1	0.0	0.33	0.09	0.56	0.01	0.28
0	0		8	55	6	0		4	8
Pd	Yb%	Ag%	Pb	Rb	Au%	As%	Os%	Re%	Y%
%			%	%					
0	0	0	0	0	0	0	0	0	0

Table 5. elemental content of Sample 4.

 Table 6. elemental content of Sample 5.

Mg	Al%	Si%	S%	K%	Ca%	Ti%	V%	Cr%	Mn%
%									
0.63	1.42	5.95	1.01	2.01	82.08	0.382	0.040	0.042	0.079
Fe%	Cu%	Zn%	Sr%	Zr%	Ru%	Eu%	Yb%	Hg%	Ba%
4.23	0.07	0.030	0.95	0.04	0.528	0.06	0.01	0.02	0.40
	8		7	2					
Ni%	Pd%	Ag%	Pb%	Rb%	Au%	As%	Os%	Re%	Y%
0	0	0	0	0	0	0	0	0	0

Mg	Al%	Si%	S%	K%	Ca%	Ti%	V%	Cr%	Mn
%									%
0.5	0	5.95	1.2	1.8	83.3	0.29	0.05	0.05	0.05
4			8	5	7		3	8	8
Fe%	Cu%	Zn%	Sr%	Zr%	Ru%	Eu%	Ba%	Hg%	Ni%
3.5	0.05	0.018	1.2	0.0	0.40	0.09	0.56	0.01	0.47
7	2		9	65	4	1			8
Yb	Pd%	Ag%	Pb	Rb	Au%	Re%	Os%	As%	Y%
%			%	%					
0	0	0	0	0	0	0	0	0	0

 Table 7. elemental content of Sample 6.

 Table 8. elemental content of Sample 7.

Mg%	Al%	Si%	S%	К%	Ca%	Ti%	V%	Cr%	Mn
									%
0.61	1.42	6.72	1.6	1.8	81.0	0.33	0.04	0.05	0.06
			9	8	3	9	7	8	3
Fe%	Cu%	Zn%	Sr%	Zr%	Ru%	Eu%	Ba%	Hg%	Ni%
3.90	0.03	0.008	1.1	0.0	0.32	0.06	0.50	0.01	0.12
	9	1	2	48	0			7	
Re%	Yb%	Ag%	Pb	Rb	Au%	0 s%	As%	Pd%	Y%
			%	%					
0	0	0	0	0	0	0	0	0	0

 Table 9. elemental content of Sample 8.

Mg %	Al%	Si%	S%	K%	Ca%	Ti%	V%	Cr%	Mn%
0.86	1.34	6.62	1.44	1.64	80.86	0.298	0.052	0.054	0.054
Fe%	Cu%	Zn%	Sr%	Zr%	Ru%	Eu%	Ni%	Hg%	Ba%
3.65	0.622	0.386	1.06	0.05 1	0.30	0.10	0	0.005	0.57
Re%	Yb%	Pb%	Os%	As%	Pd%	Ag%	Rb%	Au%	Y%
0.00	0.004	0.037	0.01	0.00	0	0	0	0	0
1			0	2					

Mg	Al%	Si%	S%	K%	Ca%	Ti%	V%	Cr%	Mn
%									%
0.5	1.21	6.21	2.8	3.1	79.1	.368	0.04	0.15	0.08
5			1	6	6		1	3	8
Fe%	Cu%	Zn%	Sr%	Zr%	Ru%	Ba%	Yb%	Hg%	Rb%
4.0	0.05	0.010	1.1	0.0	0.41	0.43	0.00	0.02	0.02
8	2		5	51	2		8	3	3
Re	Ni%	Pb%	Os	As	Pd%	Ag%	Eu%	Au%	Y%
%			%	%					
0	0	0	0	0	0	0	0	0	0

Table 10. elemental content of Sample 9.

 Table 11. elemental content of Sample 10.

Mg	Al%	Si%	S%	K%	Ca%	Ti%	V%	Cr%	Mn
%									%
0.6	1.55	6.99	1.9	2.0	80.0	0.32	0.05	0.05	0.05
6			9	3	8	7	2	6	9
Fe%	Cu%	Zn%	Sr%	Zr%	Ru%	Eu%	Yb%	Hg%	Re %
4.0	0.03	0.008	1.1	0.0	0.30	0.08	0.01	0.02	0.00
0	9		7	50	3	8			1
Ва	Ni%	Pb%	Os	As	Pd%	Ag%	Rb%	Au%	Y%
%			%	%					
0	0	0	0	0	0	0	0	0	0

 Table 12. elemental content of Sample 11.

Mg	Al%	Si%	S%	К%	Ca%	Ti%	V%	Cr%	Mn
%									%
0.5	1.37	6.70	1.5	1.5	81.4	0.35	0.04	0.05	0.06
3			6	3	5	9	7	0	8
Fe	Cu%	Zn%	Sr%	Zr%	Ru%	Eu%	Ba%	Hg%	Ni%
%									
4.0	0.04	0.01	1.1	0.0	0.34	0.06	0.48	0.02	0.07
8	2	0	8	49	6			1	2
Yb	Re%	Pb%	Os	As	Pd%	Ag%	Rb%	Au%	Y%
%			%	%					
0	0	0	0	0	0	0	0	0	0

Mg %	Al%	Si%	S%	К%	Ca%	Ti%	V%	Cr%	Mn%
0.90	4.83	16.0	0.9 31	2.4 1	56.83	1.38	0.090	0.11	0.27
Fe%	Cu%	Zn%	Sr%	Zr%	Ru%	Eu%	Pd%	Hg%	Ni%
14.5 7	0.07 8	0.01	0.3 66	0.1 0	0.715	0.13	0	0.03	0.06 0
Re%	Au%	Pb%	Y%	Os %	As%	Ba%	Ag%	Rb%	Yb%
0.05	0.04 7	0.046	0.0 19	0	0	0	0	0	0

Table 13. elemental content of Sample 12.

 Table 14. elemental content of Sample 13.

Mg	Al%	Si%	S%	К%	Ca%	Ti%	V%	Cr%	Mn
%									%
0.7	1.80	9.23	0.9	1.8	76.1	0.62	0.04	0.07	0.11
5			53	4	4	3	4	6	
Fe%	Cu%	Zn%	Sr%	Zr%	Ru%	Eu%	Ba%	Hg%	Ni%
6.2	0.07	0.028	0.9	0.0	0.51	0.07	0.40	0.02	0.06
32	6		26	62	2			2	6
As	Pb%	Rb%	Yb	Re	Ag%	Os%	Au%	Pd%	Y%
%			%	%					
0.0	0.02	0.016	0	0	0	0	0	0	0
06	2								

 Table 15. elemental content of Sample 14.

Mg	Al%	Si%	S%	К%	Ca%	Ti%	V%	Cr%	Mn%
70									
0.62	1.50	6.49	1.63	2.20	80.71	0.337	0.053	0.085	0.061
Fe%	Cu%	Zn%	Sr%	Zr%	Ru%	Eu%	Ba%	Hg%	Ni%
4.05	0.13	0.067	1.02	0.05	0.308	0.087	0.56	0.015	0
	5	7		0					
Yb%	Os%	Pb%	Rb%	As%	Re%	Ag%	Y%	Au%	Pd%
0.00	0.01	0	0.01	0	0	0	0	0	0
			3						

Mg %	Al%	Si%	S%	К%	Ca%	Ti%	V%	Cr%	Mn%
0.6	1.20	6.07	1.6	1.5	82.4	0.31	0.05	0.05	0.05
2			1	8	3	5	5	5	8
Fe%	Cu%	Zn%	Sr%	Zr%	Ru%	Eu%	Ba%	Hg%	Ni%
3.6	0.04	0	1.1	0.0	0.34	0.09	0.58	0.01	0
7	3		3	52	2	3		8	
Lu%	Au%	Pb%	Yb	As	Re%	Ag%	Os%	Au%	Pd%
			%	%					
0.0	0.02	0.01	0.0	0	0	0	0	0	0
2	9		09						

Table 16. elemental content of Sample 15.

 Table 17. elemental content of Sample 16.

Mg	Al%	Si%	S%	К%	Ca%	Ti%	V%	Cr%	Mn%
%									
0.53	1.23	5.98	1.99	1.75	81.77	0.337	0.046	0.052	0.05
									5
Fe%	Cu%	Zn%	Sr%	Zr%	Ru%	Eu%	Yb%	Hg%	Ni%
3.84	0.15	0.084	1.11	0.05	0.338	0.10	0.035	0.01	0
	8	8		3					
Pb%	Ba%	As%	Os%	Au	Re%	Ag%	Rb%	Y%	Pd%
				%					
0.02	0.51	0.003	0	0	0	0	0	0	0

The tables of elemental content show high content of calcium, iron and silicon in general, low content of mercury, lead, gold and silver as well as many other elements, and moderate content of aluminum, titanium, magnesium,

Quantitative analysis

- Standard Solutions
- 1- Standard Lead Solution (100 μ g/ml): this solution was prepared by dissolving of 0.0159 g of lead nitrate in sufficient deionized water to make exactly 100ml in a volumetric flask.



Table 18. The accuracy and precision of thecalibration curve of standard lead solution

Concentration (µg/ml)	RSD%	Error%	
0.05	6.91	0.22	
0.5	0.45	0.03	
1.0	6.88	0.41	

Figure 3. The calibration curve of Lead

2- Standard Zinc solution (100 μg/ml): this solution was prepared by dissolving 0.0390 g of hydrolyzed Zinc acetate () in sufficient deionized water to make exactly 100 ml using volumetric flask.



Figure 4. The calibration curve of Zinc

Table 19. The accuracy and precision of the
calibration curve of standard znic solution

Concentration of Zn (µg/ml)	RSD%	Error%
0.05	0.88	0.22
0.1	0.65	0.03
0.5	2.04	0.41

3-Standard Iron Solution (100 μ g/ml): this solution was prepared by dissolving 0.0290 g of Ferric chloride in sufficient deionized water to make exactly 100 ml using volumetric flask.



Table 20. The accuracy and precision of thecalibration curve of standard Iron solution

of iron(µg/ml)	RSD%	Error%
10	2.41	0.22
20	0.42	0.03
30	0.10	0.41

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Figure 5. The calibration curve of Iron

4-Standard Nickel Solution (100 μg/ml): this solution was prepared by dissolving 0.0447 grams of aqueous Nickel Sulfate in sufficient deionized water to make exactly 100 ml using volumetric flask. Table 21. The accuracy and precision of the

calibration curve of standard nickel solution



Concentration of nickel (µg/ml)	RSD%	Error%
20	0.21	6.3
30	1.01	3.9
40	0.058	4.17

Figure 6. The calibration curve of Iron

3- Quantitative analysis

The selected elements have been estimated using atomic absorption device, table 22 show the results.

Sample				Elemental content (µg/ml)				
	Zn	Pb	Fe	Ni	Со	Cd		
1	0	0	37.59	025.1	0	0		
2	0	0.035	66.04	1.626	0	0		
3	0.0181	0	55.71	2.418	0	0		
4	0	0	59.71	2.460	0	0		
5	0	0.232	53.28	2.875	0	0		
6	0	0	2.527	2.720	0	0		
7	0.0896	0	5.195	2.826	0	0		
8	0	0	69.19	3.073	0	0		
9	0	0.282	44.96	2.720	0	0		
10	0	0.057	60.66	2.526	0	0		
11	0.0049	0	52.90	2.660	0	0		
12	0	0	68.90	2.538	0	0		
13	0.0982	0.16	5.074	1.846	0	0		
14	0.5771	0.25	61.52	2.026	0	0		
15	0.0956	0.078	55.66	1.800	0	0		
16	0.7555	0.555	53.95	1.286	0	0		

Table 22. Quantitative analysis

Table 22 indicate the presence of high concentration of iron in all samples, and 72.52 μ g/ml in sample 6 as a maximum level to 37.59 μ g/ml in sampl1 as a minimum level. Nickel was ranged between 1.025 μ g/ml in sample 1 to 2.875 μ g/ml in sample 5. The highest zinc content was detected in sample 16 and it was 0.7555 μ g/ml. Cobalt and cadmium were not detected in all samples.

Conclusion

sixteen samples of dust deposits are collected from indoor and outdoor of the two Badoush Cement Factory Expansion and the New Badoush Cement Factory in Mosul city. The aim of the research is identification and estimating the concentrations of the heavy metals in the dust samples emitted from the two Factories. The results show high content of iron, and relatively nickel, while cobalt and cadmium were not detected.

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