COMPLEX CHARACTERISATION OF SPENT HOUSEHOLD BATTERIES WITH Zn AND Mn CONTENT FOR RECOVERING OF NONFERROUS METALS

Simona SĂCEANU[1], Mariana CIURDAŞ[2], Gabriela POPESCU[3], Mihai BUZATU[4]

General purpose batteries contain many metals in high concentration, metals that can be recovered and reused instead of being diluted in municipal incinerators or to be deposited on wastes. Collected batteries contain significant amounts of toxic metals, including mercury, which prevents direct recycling of batteries in secondary metals industry. In the years 1995-1996 only two battery recycling plants were functional in Switzerland but with very high costs. The paper presents a detailed physical-chemical characterization of household batteries discarded in order to set up a series of cheap and "clean" manufacturing processes of these waste. Pilot scale tests, with several tones of batteries, have demonstrated opportunities to reduce costs and thus the feasibility of technology. Using this method of proper equipment assures the costs in case of transposition process on industrial scale.

1. Introduction

Over 90% from all household batteries collected in European union are estimated to be recycled. These percentage varies from country to country and depends of the batteries type [1]. For exemple:

- almost 100% of NiCd collected batteries are recycled;
- in case of universal use batteries (alkaline ones with Mn and Zn-C) the situation is different between countries:
    - in some countries most household collected batteries are sent to a recycling facility (Austria, Belgium, France, Netherlands);
    - in other countries only 60-65% of collected batteries are sent to a recycling facility (Denmark, England, Swseden);
    - in the remaining countries are not estimated recycled quantities.

[1] Ph.D. student, Materials Science and Engineering Faculty, University POLITEHNICA of Bucharest, Romania, e-mail: catrina_simona@yahoo.com
[2] Lecturer, Materials Science and Engineering Faculty, University POLITEHNICA of Bucharest, Romania, e-mail: ciurdasmariana@yahoo.com
[3] Prof., Materials Science and Engineering Faculty, University POLITEHNICA of Bucharest, Romania, e-mail: gabriela.popescu@.upb.ro
[4] Prof., Materials Science and Engineering Faculty, University POLITEHNICA of Bucharest, Romania, e-mail: buzatu.mihai@yahoo.com

Recycling rate limiting of universal hosehold batteries in some countries is motivated from different reasoning. Relatively high content of mercury in universal household batteries, entered on the market before the entry into force of EU legislation (that provide restrictions about batteries that contain Hg, others than the type pill), are not recycled totally in some countries due to specific cost of recycling (in Germany the main collector GRS give an average content of Hg in ZnC + AlMn batteries of 60 ppm in 1998, 100 ppm in 2002 and 10 ppm in 2005).

Universal household hazardous batteries (i.e. those that doesn't contain Hg) in some countries are disposed in wastes. Button batteries containing up to 30 wt% Hg are recycled in specialized equipments; some of them have possitive market value (e.g. those containing Ag), others have a negative market value, the global value becomes negative. As for lithium-ion batteries the specialized processes are in progress and must be done safely (risk of explosion and fire in the manufacture and recycling being high). At this moment most amounts of collected parts are stored attempted that recycling processes to be available. Other rechargeable or non-rechargeable batteries (like NiMH, Li) at this moment are not recycled. Collected batteries that are not recycled are deposed in wastes as hazardous waste or dangerous waste depending on their type.

Before recycling the batteries must be sorted by categories:

- ZnC and alkaline batteries;
- NiCd batteries;
- Acid lead household batteries;
- Button batteries;
- Lithium batteries;
- Li-Ion batteries.

There are sorted equipments in all the countries where separate collection are developed (1 to 3 equipments according to the country size and the quantities of collected batteries). As for recycling, the batteries are recycled in facilities for the small batteries recycling, in melt metallurgical plants or in electric arc furnace (EAF) [1,2,3].

In E.U. are about 32 plants specialized on the recycling of batteries and are concentrated in certain countries (mostly in Germany and France). More specific systems for recycling of household batteries are used under their capacities (up to half of their capacity) so there is overcapacity of recycling. In this case after collection, the used batteries are transported from countries without any recycling facilities in countries where there is overcapacity for recycling.

Reports on recycling rates can be easily misinterpreted. The fraction of recycled material consists of three fractions: *fraction of sold batteries* that are returned, *fraction of recover material* from each battery separately and *fraction of* *material actually recovered*. Finally, can be reach an effective recovery located between 39-90% of the total weight of the battery.

2. Analysis of battery components

Component analysis of alkaline batteries (with Zn and Mn content) was done by their manual dismantling. Batteries were opened by slitting the outer casing of the battery using a metal cutting saw. The content was removed and separate so that the anodic paste components with Zn-ZnO-KOH and the cathodic paste with Mn-C-KOH can be analyzed separately and then like a mixture obtained by mixing later.

Steel shell and current collector rods from brass or graphite were carefully removed so that the battery contents are not contaminated with other metals.

Alkaline battery components are shown in Figs. 1, 2 and 3 and components weight in table 1.

(a) (b)

Fig 1. Alkaline battery electrodes: a) cathode b) anode

(a) (b)

Fig.2. Metallic component: a) cathode current collector; b) anode current collector from bronze; ex. battery case, terminal ends, steel separators.

(a) (b) (c)

Fig. 3. Plastic, paper, cardboard:
a) outer sleeves; b) support elements; c) separators in paper and cardboard insulators.

Table 1

Weight components of AA alkaline batteries

Component	Material	Weight g/battery	Weight %
Anode head	Steel	0.29	1.34
Isulator	Cardboard	0.06	0.28
Supporting element	Polyamide (PA)	0.21	1.00
Metallic separator	Steel	0.38	1.75
Anode current collector	Bronze	0.50	2.32
Cathode current collector (battery case)	Steel	4.20	19.52
Separator	Paper	0.10	0.50
	Cellophane	0.04	0.21
Plastic outer sleeve	PVC	0.23	1.07
Negative electrode (white paste - anode)	Zn + ZnO + KOH	4.46	20.72
Positive electrode (black paste - cathode)	MnO_2 + C + KOH	9.10	42.29
Humidity		1.94	9
TOTAL	-	21.52	100
Full battery	-	22.80	
Cutting losses	-	1.18	

Zn-C battery components (with Zn and Mn content) are presented in Figs. 4, 5 and 6, and weight of components in table 2.

Chemical composition of active mass (black cathodic paste), white anodic paste) for different types of batteries is presented in table 3.

(a) (b)

Fig. 4. Zn-C battery electrodes:
a) cathode; b) anode

(a) (b)

Fig. 5. a) Iron housing and terminal ends; b) cathode current collector from graphite.

(a) (b)

Fig. 6. a) Paper, cardboard; b) plastic.

3. Physical-chemical characterization of used batteries with Zn and Mn content

It was determined the chemical composition of 20 types of batteries (< 70 g) that are on the market.

In table 4 is presented the chemical composition for different types of batteries with Zn and Mn content, and in table 5 the chemical composition of cathodic and anodic paste.

Table 6 presents the chemical composition of paste for electrodes (cathodic and anodic paste) for different types of consumed batteries.

Table 7 presents the chemical composition for different types of button consumed batteries.

Table 2

Components weight for different Zn-C batteries

Battery Components	Battery type							
	AA		C		D		D	
	(g)	(%)	(g)	(%)	(g)	(%)	(g)	(%)
Entire battery	**17.1**	**100**	**46.7**	**100**	**81.6**	**100**	**97**	**100**
Cutting losses	0.03	0.18	0.5	1.07	0.07	0.09	0.06	0.06
Paper	0.66	3.86	8.03	17.19	3.85	4.72	12.7	13.09
Steel	1.84	10.76	1.82	3.90	3.87	4.74	3.49	3.60
Negative electrode (zinc house-anode)	3.15	18.42	7.75	16.60	11.7	14.34	16.2	16.70
Cathode current collector (rod – C)	1.1	6.43	2.2	4.71	4.2	5.15	4.75	4.90
White paste (anode)	1.85	10.82	2.1	4.50	4.65	5.70	5.51	5.68
Positive electrode (black paste-cathode)	5.64	32.98	15.9	34.05	38.86	47.62	37.79	38.96
Humidity	2.83	16.55	8.4	17.99	14.4	17.65	16.5	17.01

Table 3

Chemical composition of electrodes (cathodic paste, anodic paste) for different types of batteries (with Zn and Mn content)

Element	Battery type		
	Alkaline (AA+AAA)		Zn-C (A+AAA+C+D)
	Cathodic Paste (MnO_2+C+KOH)	Anodic Paste (Zn+ZnO+KOH)	Cathodic Paste (MnO_2+C+NH_4Cl/$ZnCl_2$)

	%	%	%
Mn	41.30	0.56	26.60
Zn	10.00	74	27.40
Al	0.03	0.009	0.050
B	0.02	0.003	0.010
Cd	0.0004	0.0001	0.0001
Cr	0.012	0.007	0.017
Cu	0.032	0.026	0.030
Fe	0.10	0.043	0.39
Ni	0.005	0.001	0.001
Pb	0.010	0.020	0.05
Si	0.065	0.070	0.13
Ti	0.017	0.002	0.004
K	4.63	5.05	0.033

Table 4

Chemical composition for different types of spent batteries (with Zn and Mn content)

No.	Battery type	Total weight, g	Chemical composition,[%]				
			Zn	Mn	Fe	Cd	Hg
1	9 V	46.216	6.96	1.48	15.96	<0.0002	0.0005
2	9 V	36.171	9.54	14.7	20.4	<0.0002	0.0005
3	9 V	36	10.11	12.56	19.71	<0.0002	0.0006
4	1.5 V R20	69.352	20.3	6.98	1.33	0.1102	0.0056
5	1.5 V R6	17.831	29.27	13	19.98	<0.0002	0.0005
6	1.5 V R6	17.241	30.4	16.27	20.53	<0.0002	0.0005
7	1.5 V R6 alkaline	22.835	18.28	18.82	19.81	<0.0002	0.0004
8	1.5 V R6	15.827	28.15	16.75	20.22	0.0003	0.0015
9	1.5 V R6	18.207	26.29	10.62	20.41	0.0003	0.0005
10	1.5 V R6	17.548	26.84	15.91	20.75	0.0004	0.0005
11	1.5 V R6	17.67	25.35	13.88	21.01	<0.0002	0.0003
12	1,5 V R6	18,701	26,2	13,48	19,53	<0,0002	<0,0002
13	1.5 V R6 alkaline	21.808	18.64	21.36	19.16	<0.0002	0.0171
14	1.5 V R6	18.115	25.97	15.04	23.58	0.0028	0.0007

Table 5

Chemical composition of the metallic coat for different types of spent batteries

No.	Battery type	Weight cover, g	Chemical composition, [%]				
			Zn	Mn	Fe	Cd	Hg
1	9 V	8.210	0.47	0.26	65.8	<0.0002	0.0019
2	9 V	9.116	2.65	0.18	80	<0.0002	0.0014
3	9 V	8.348	2.86	0.26	77.9	<0.0002	0.0013
4	1.5 V R20	23.96	51.5	0.61	1.75	0.026	0.013
5	1.5 V R6	3.85	0.35	0.42	91.7	<0.0002	0.0018
6	1.5 V R6	4.618	11.7	0.71	76.6	<0.0002	0.0014
7	1.5 V R6 alkaline	5.974	3.26	1.31	74.9	<0.0002	0.0009
8	1.5 V R6	3.659	0.24	0.21	87,5	0.0003	0.0043
9	1.5 V R6	3.944	0.11	0.23	91	0.0003	0.0015
10	1.5 V R6	3.877	0.19	0.23	93	0,0004	0.0016
11	1,5 V R6	3,908	0,087	0,24	95,2	<0,0002	0,0008
12	1.5 V R6	3.948	0.15	0.28	92.3	<0.0002	<0.0002
13	1.5 V R6 alkaline	5.205	2.56	0.56	76.6	<0.0002	0.0033
14	1.5 V R6	4.362	0.31	0.41	96.3	0.003	<0.0002

Table 6

Chemical composition of paste for electrodes (cathode and anode) for different types of spent batteries

No.	Battery type	Paste weight, g	Chemical composition, [%]				
			Zn	Mn	Fe	Cd	Hg
1	9 V	36.231	8.75	1.82	5.46	<0.0005	0.0002
2	9 V	25.877	12.4	20.5	0.34	<0.0005	0.0002
3	9 V	26.585	12.8	17	2.22	0.00014	0.0003
4	1.5 V R20	38.528	4.49	12.2	1.32	0.0021	0.0021
5	1.5 V R6	13.395	38.9	17.3	0.24	<0.0002	<0.0002
6	1.5 V R6	11.92	40.9	23.4	0.045	<0.0002	<0.0002
7	1.5 V R6 alkaline	16.258	24.5	26.1	0.3	<0.0002	<0.0002
8	1.5 V R6	11.498	38.7	23	0.033	0.0003	0.0007
9	1.5 V R6	13.747	34.8	14	0.94	0.0003	<0.0002
10	1.5 V R6	13.259	35.5	21	0.2	0.0005	0.0002
11	1.5 V R6	13.286	33.7	18.4	0.016	<0.0002	<0.0002

12	1.5 V R6	14.273	34.3	17.6	0.039	<0.0002	<0.0002
13	1.5 V R6 alkaline	16.247	24.2	28.5	1.29	<0.0002	<0.0022
14	1.5 V R6	12.723	36.9	21.3	0.54	0.0009	0.004

Table 7

Chemical composition for different types of button batteries

	Weight [g]	Hg %	Cd %	Ni %	Mn %	Zn %	Fe %	Cr %	Cu %	Pb %	Al %
A	3.002	0.0065	<0.0001	3.21	17.9	<0.001	43.1	9.33	0.085	<0.0005	0.006
B	3.166	0.0038	<0.0001	2.87	18.4	<0.001	40.0	8.80	0.044	<0.0005	0.006
C	1.932	0.73	<0.0001	1.23	16.6	8.00	43.0	0.009	0.016	0.033	0.015
D	1.910	0.75	0.076	1.51	15.5	9.45	53.0	0.008	0.006	0.11	0.014
E	0.645	0.66	0.003	1.67	13.8	7.95	53.5	0.007	0.009	0.066	0.034
F	0.300	0.33	0.00025	1.95	8.75	6.92	60.5	0.020	0.008	0.078	0.034

The methods used for chemical analysis of batteries, with Zn and Mn content, were: Plasma Optical Emission Spectrometry: DCP for Hg (λ = 253.652 nm) and Cd (λ = 228.802 nm), and ICP to determine the chemical composition. For batteries with weight of 15-70 g only Fe, Mn and Zn had significant values for recoveries. At batteries >15g could effectively separate the outer shell (metallic Fe for majority or Zn) of cathodic and anodic paste and the plastic isolation.

Does not detected mercury in batteries containing Zn and Mn (alkaline and Zn-C) because it was successfully removed in 1994, when producers started to release on the market free mercury batteries.

It was determined experimentally the composition of Duracell type alkaline batteries (with Zn and Mn content) by manual dismantling.

The AA and D size batteries were opened by slitting the outer casing of the battery with a metal cutting saw. The content was removed and separate so that components of anodic paste with Mn and cathodic paste with Mn and C can be analyzed separately and then the mixture is obtained by mixing later.

Brass steel shall and current collector rods were carefully removed manually so battery content not contaminated with other metals.

Weight components and chemical composition are presented in table 8 and 9.

Table 8

Component distribution of Duracell alkaline batteries by category

Component	20 alkaline battery Duracell D		20 alkaline battery Duracell AA	
	g	%	g	%
Housing	167	12.16	54.5	24.94
Plastic + metal cased catch	96	6.99	8.5	3.89
Cathode: MnO_2/C paste	744	54.17	103	47.14
Anode: Zn paste	366.5	26.68	52.5	24.03

Table 9

Chemical composition of cathodic, anodic paste and their mixture for Duracell alkaline batteries

Element	Mn/C cathodic paste	Zn anodic paste	Mn/C/Zn Paste mixture
Mn	44%	-	29%
Zn	-	51%	18%
C	56%	-	38%
Ni	0.002%	-	-
Cu	0.001%	-	-
Fe	0.05%	-	-

Small concentrations of other metals in anodic and cathodic paste and their mixture will not be in case for batteries processed in a shredder or mill.

Chemical composition of unlike large batteries for vehicles and household batteries are very different . Depending on the size and shape we can sort them by categories, and according to chemical composition can determine which metals can be recovered from each category, that can be treated together and separately. For example, household batteries (alkaline MnO_2 and saline Zn-C) which represents 83% of total household batteries collected contain the same metals Mn and Zn (thus can be processed together and separatelly) in high concentrations which can be recovered and reused, instead of being incinerated in municpal incinerator wastes or be deposited on wastes.

Spent household batteries are no longer what they were at first. Their have changes them both physically and chemically. Electrodes, for example, can deform and corrode occuring unavoidable leaks, and chemical reactions doesn't occur.

In Fig. 7 is presented a Zn-C battery in different stages of corrosion.

Fig. 7. Corrosion of a Zn-C battery AAA type: a) new batteries; b,c) spent batteries

By XRD analysis were analised changes suffered by those minerals contained in batteries with Zn and Mn content, during their discharge. From the diagram is remarked the presence of Mn and Zn oxides. We notice the presence of $ZnMn_2O_4$ compounds obtained by combining oxides: ZnO, MnO and MnO_2. The presence of $KHCO_3$ (Kalicinite) is attributed to the reaction of KOH with CO_2 from atmosphere that occurs during cathodic paste dismantling, breakage and drying.

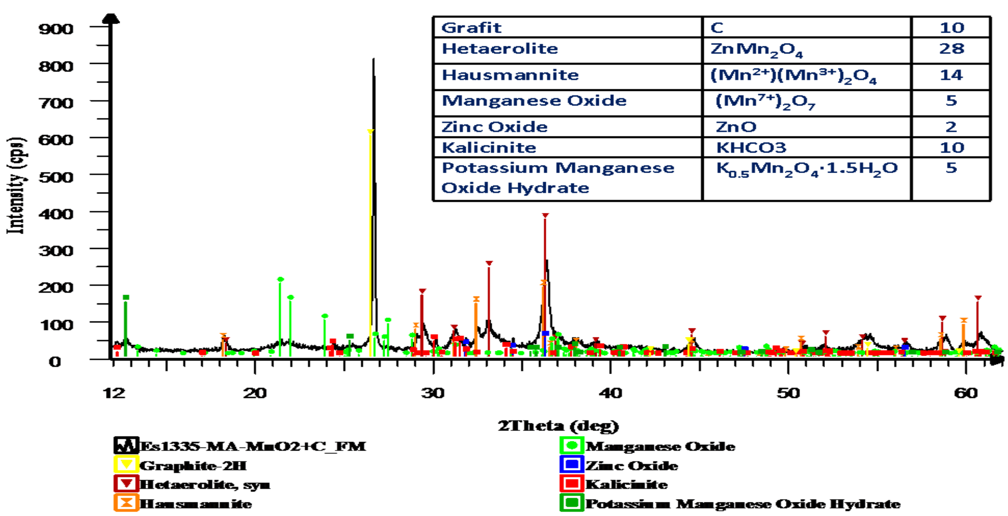

Fig. 8. Semi quantitative analysis of cathodic paste, alkaline batteries

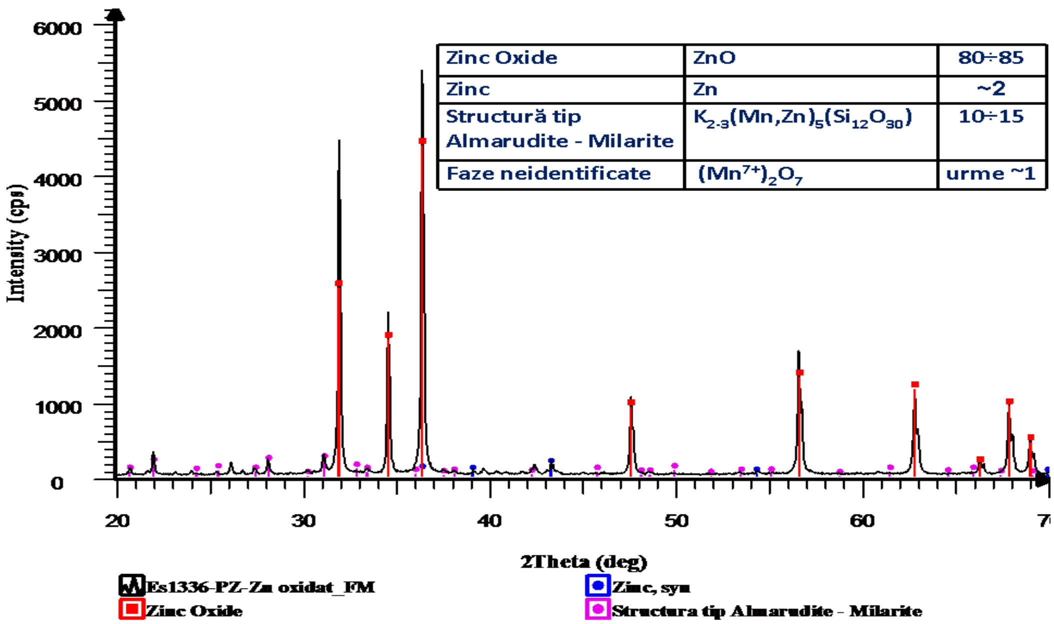

Fig. 9. Semi quantitative analysis of anodic paste, alkaline batteries

XRD diagram for cathodic paste obtained from crushing of spent Zn-C batteries is shown in Fig. 10.

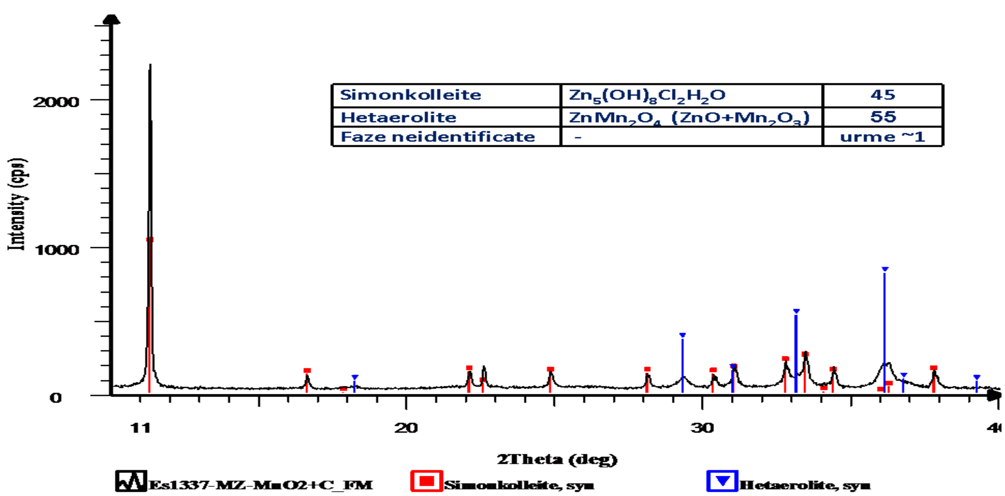

Fig. 10. Semi quantitative analysis of cathodic paste, Zn-C batteries

Formation of $Zn_5(OH)_8Cl_2{\cdot}(H_2O)$ in used Zn-C batteries is attributed to the hydrolysis of $ZnCl_2$ in the electrolyte (electrolyte composition being 26% NH_4Cl, 8.8%$ZnCl_2$, and 65.2%H_2O) according to reactions at the cathode:

$$2NH_4^+ + 2MnO_2 + 2e^- \rightarrow Mn_2O_3 + H_2O + 2NH_3 \quad (1)$$

$$5ZnCl_2 + 8NH_3 + 9H_2O \rightarrow Zn_5(OH)_8Cl_2{\cdot}(H_2O) + 8NH_4Cl \quad (2)$$

And the reaction between the $ZnCl_2$ form the electrolyte and ZnO formed at the anode:

$$Zn \rightarrow Zn^{2+} + 2e^- \quad (3)$$

$$ZnCl_2 + 4ZnO + 5H_2O \rightarrow Zn_5(OH)_8Cl_2{\cdot}(H_2O) \quad (4)$$

4. Conclusion

Based on our results, we make the following conclusions.

- In this work, we have investigated the chemical composition of different type of spent household batteries like: Zn- C, AA, AAA, C or D size batteries and 9 V rectangular batteries.
- Spent household batteries may have heavy metals when disposed of in landfills. The type of battery can influence the concentrations of heavy metals in the anodic and cathodic paste.
- Zinc–carbon batteries and alkaline batteries released high amounts of Zn and Mn.
- When battery size was taken into account, the D size zinc–carbon and alkaline batteries released higher concentrations of Cd, Mn, and Zn, in comparison to other sizes.
- An quantitative analysis was performed, and the mass concentration of the identified metal presents in cathodic/anodic paste from alkaline batteries shows the presents of Zn, Mn oxides like: ZnO, Mn_2O_7, Zn Mn_2O_4.

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