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EXTRACTION OF ZINC SULFATE THAT UTILIZES IN THE MANUFACTURING OF FOOD SUPPLEMENTS BY USAGE (ZN-C) BATTERIES WASTES

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Abstract: Spent zinc-carbon (dry cell) batteries have negative environmental effects. It is necessary to save the environment from them and take back the mineral values from these batteries. Many engineering materials were contained in the spent batteries. A large amount of anode zinc (zinc casing) was occupied in spent batteries, therefore; it must be recovered on the form of a useful and essential chemical compounds that can be used in daily life. It is found from the chemical composition an anode zinc (zinc casing), it was over 99 percent perspicuous with a very small percentage of traces metals in it. Zinc sulfate was known as a significant food supplement for humans, animals and plants. It can be made by investing the selective corrosion resulted from the chemical reaction between zinc metal and diluted sulfuric acid. Thus, the zinc sulfate heptahydrate was produced. Zinc sulfate heptahydrate resulted from corrosion reactions was tested by XRD and it was found similar to standard patterns. The XRD pattern of zinc sulfate heptahydrate shows four major peaks happened at (2Ɵ). The most intense peak for zinc sulfate heptahydrate happened at 27.5°. In addition, to hydrogen gas was produced as a by-product of that reaction.

Keywords: *Zn-C battery, Zinc waste, Food supplements, Nutritional support and Zinc sulfate.*

1. Introduction

1.1. Human Blood and Minerals

The diet must be contained necessary minerals and trace elements because they perform significant physiological functions within the human body and this is evident in Table1.The North American Institute of Medicine has founded reference classifications for many food-derived minerals and their relationship to age groups. It is worthless that eating few minerals will lead to a decrease in minerals, and that an increase in mineral intake will cause poisoning. That is, inappropriate intake of minerals in the human body, whether because of disease or poor absorption, will lead to mineral deficiency, and incorrect and excessive intake will lead topoisoning. There are many minerals that its deficiency or toxicity cannot be diagnosed until after days has passed, and then clinical symptoms and signs will become clear on the patient [1].

1.2. Nutritional Supports or Food Supplement

Dietary supplements are defined by the European Union (EU) as a group of nutrients that provide a natural diet. They are concentrated sources of minerals and other materials with a nutritional or physiological influence, individually or in combination, and are marketed in many forms, such as capsules, tablets, powder sachets, liquid ampoules, and bottles [2]. Food supplements marketed in the European Union must be subject to the food legislation in the European Union in terms of their composition, manufacture and control [2].

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Since nutritional supplements are designed to provide accurate nutrients and minerals, specialized and delicate skills and equipment must be used [2].

It is a group of vitamins, minerals and proteins that are used to give the need of the body of food, whether these needs therapeutic or simply to improve the performance of a specific function in different sports or personal reasons related to the same person and in spite of the benefit that provided by supplements, but there are those who use it wrongly to obtain on the results of rapid and effective, which causes damage may be serious in some cases so all countries seek to systemize the use of these materials and strict control of production and trafficking[3].

The bodies need minerals in different amounts according to the mineral type. There is a trace minerals, such as iron, molybdenum, zinc, selenium and iodine, are needed by our bodies only in a few milligrams or less, while large minerals, such as potassium, calcium, magnesium, phosphorous and sodium, are needed in the hundreds of milligrams, these minerals have an important role in the body. Many minerals influence enzymatic functions, and some are used to keep the balance of body fluids, build bone tissue, systemize hormones, transmit nerve impulses, contract and relax muscles, and protect against harmful free radicals (cancer cells). Table1 shows the minerals and their main functions [3].

Table1. The minerals and their major functions [3].

Minerals	Major Functions
Sodium	Fluid balance, stomach acid production
Chloride	Fluid balance, nerve transmission, muscle contraction
Potassium	Bone and teeth health maintenance, nerve transmission, muscle, contraction, blood clotting
Calcium	Bone and teeth health maintenance, acid-base balance
Phosphorus	Protein production, nerve transmission, muscle contraction
Magnesium	Protein production, nerve transmission, muscle contraction
Sulfur	Protein production
Iron	Carries oxygen, assists in energy
Zinc	Protein and DNA production, wound healing, growth, immune system function
Iodine	Thyroid hormone production, growth, metabolism
Selenium	Antioxidant
Copper	Coenzyme, iron metabolism
Manganese	Coenzyme

1.3. Zinc Sulfate and Zinc Sulfate Supplement

Zinc sulfate is considered as a food supplement and it is an inorganic compound. This compound is used to heal zinc lack, where a lack of zinc causes a great risk. Zinc sulfate has a white powdery appearance, as shown in Figure1 [4]. The side effects of increasing zinc sulfate supplementation are abdominal pain, vomiting and fatigue. Zinc sulfate has the chemical formula $ZnSO_4$. It was previously known as "white vitriol". One kind of zinc sulfate are in the shape of colorless solid material, it is Zinc Sulfate Anhydrous [4]. There are four kinds of zinc sulfate as; zinc sulfate anhydrous $ZnSO4$, zinc sulfate monohydrate $ZnSO_4.H_2O$, zinc sulfate hexahydrate $ZnSO_4.6H_2O$ and zinc sulfate heptahydrate $ZnSO_4.7H_2O$. The most common one is zinc sulfate heptahydrate $ZnSO_4.7H_2O$ and is known as goslarite. Zinc sulfate anhydrous is not found naturally [4][5]. Zinc sulfate is considered as a medical treatment as it is used in combination with oral rehydration therapy (ORT) and an astringent drug [4].

Figure 1. Zinc Sulfate Anhydrous [4].

Poisoning with zinc sulfate teases the eyes. And that, eating few amounts of it, are considered safe, while excessive intake of large amounts of it causes a narrowing of the stomach and the appearance of nausea and vomiting. Zinc sulfate is also added to animal feed as an important basic source of zinc, at rates of several hundreds of milligrams per kilogram of feed. Zinc sulfate was produced by the reaction of mitigated sulfuric acid with the mineral zinc [4].

$$Zn + H_2SO_4 + 7H_2O \rightarrow ZnSO_4.7H_2O + \uparrow H_2 \quad (1)$$

Zinc sulfate is a significant food supplement for the human body. Priyanka Gunasekara et al. Studied the influence of zinc sulfate and multivitamins on blood sugar and lipid accumulation in adult diabetics and their control with zinc sulfate, and then estimated the influences of zinc with or without other antioxidants on blood glucose, lipid, and serum creatinine of adult diabetics with long-term follow-up [5]. Zinc sulfate has shown beneficial effects by controlling the metabolism of adult diabetics while raising the level of zinc in the blood. Zinc sulfate also resulted in good control of measured blood glucose levels at HbA1C% and HDL postprandial glucose [5].

In 2015, conclusions were drawn from the research undertaken by J.Susan and Cashman, incorrect intake of zinc sulfate and conditions including malabsorption of drugs, ultimately causes a state of lack or toxicity. The symptoms do not appear instantly, but after some days, and then the patient shows clinical signs and symptoms [1].

1.4. Corrosion and Selective Leaching Corrosion

Corrosion is damage to metal surfaces due to the chemical or electrochemical reaction between that metal and its corrosive environment surrounding it. Any mechanical damage that impacts metal surfaces without the presence of a chemical or electrochemical reaction is not considered corrosion. Corrosion does not occur with nonmetals because it affects only metal surfaces, and corrosion has different kinds according to the appearance of corrosion and its mechanism, such as general corrosion, pitting corrosion, erosion–corrosion, selective leaching corrosion (dealloying), cavitation corrosion, etc.[6].

Dealloying is a type of corrosion in which one element is selective and preferentially removed from the alloy without the rest of the casting elements. In this corrosion, there is no appreciable change in the dimensions or form of the component; But it becomes weak, brittle and porous. The preferential removal of zinc from brass alloys, is the most famous example of it; In other words, the selectively removal of the elemental zinc alone from the brass alloys by selective corrosion, leaving the copper and other elements in a weakly porous form [6].

1.5. Metal Recycling

Metal recycling is one of the important elements in the sustainable development of natural mineral resources, which contains: Reduce consumption, reuse and recycling. The recycling process goes through multiple levels that start with collecting, sorting, chemically and / or thermally treating mineral wastes to separate the desired minerals from them. In any case, the economic cost of recycling is much lower than the cost of mining and extraction processes [7]. By following the recycling processes, it will modify the economies of the governments, especially when some taxes and fees are eliminated, as well as the design and production of recyclable metal equipment [8].

Waste metals, after being recycled and converted into castings, metal products and industrial waste are invested and reused. Minerals are non-renewable natural resources and are important in agriculture, industry, medicine, pharmacy, construction, energy, space sciences and other different areas of life. The sustainable development of mineral wealth aims to consume as little as possible of the mineral reserves in mineral mines (ammunition) without a negative effect on the economic growth and the growth of the country. This occurs through the best use of mineral resources in addition to recycle metal waste, this contributes to support sustainable development that protecting the natural environment from the damages that comes with mineral extraction, this helps in preserving biological diversity and not occur the environmental pollution in the future[9,10].

The negative effects of mineral extraction consists of unsightly workings, mineral waste piles and pollution from acidic water containing heavy metals. Mineral planning at local, regional, national and EU level confirms the environment is protected and that resources are used sustainably. Recycling, reuse, and conservation of energy and mineral resources are important in achieving these goals [9, 10].

1.6. Pharmaceuticals and Nutritional Supports Synthesis

The pharmaceutical industries are among the important industries in human life and significantly enhance them. There are institutions of billions of dollars working in this field. The pharmaceutical industry includes the design and production of pharmaceuticals in all aspects of medicines, testing and delivery. Despite the fierce competition between the pharmaceutical industries, manufacturing a new cure or developing it to its final form is costly and long-term. Because of strict government controls and tests, it may take more than 10 years for a newly discovered drug to reach the market and the consumer. Of the thousands of new pharmaceutical products manufactured each year, only a certain number reach the patient [11].

And there are many pharmaceutical preparations that consist of minerals as medicine. Among the pharmaceutical preparations that use minerals in their production are food supplements in specific, intestinal antacids, adsorbents, laxatives, topical medicines or antiseptics[11]. Since mineral nutritional supplements have a quite important influence on the human body and life, so many countries are interested in the pharmaceutical industries, especially mineral nutritional supplements [2][11].

1.7. Problem of Nutritional Supports

Many young athletes take nutritional supplements to enable them to compete even though most of them know very little about what they are eating and what its side effects are. For long time, many users of nutritional supplements feel dizzy, especially wh en having nutritional supplements directly without food. Most consumers do not know is that nutritional supplements have side effects that may reach life-threatening problems or even death. For example; some nutritional supplements containing caffeine, Ephedrine or GHB (gamma hydroxy butyrate) lead to increase heart rate, headache, and increase the chances of heat stroke [1][5][11].

The nutritional supplements and stimulants have risky side effects on the heart muscle and central nervous system functions, in addition, it raises the body temperature. In 2002 nutritional supplements were a cause of death, as Douglas Page stated in the summary of his article; The increasing number of deaths among soccer players is due to heat stroke. Although nutritional supplements are not the direct cause of death, this was confirmed by Julian Bells, MD and Chair of the Department of Neurosurgery at West Virginia University [1][5] [11].

The work aims to save the environment from pollution caused by spent zinc-carbon batteries (dry cell) by recovering zinc metal and produce zinc sulfate, which is used in nutritional supplements.

2. Experimental work

2.1. Components of Zinc-Carbon Batteries

Zinc-carbon batteries were used in this work and have a cylindrical shape. They are a type of AA as shown in Figure2. The spent batteries samples have manually disassembled and the diverse parts were classified. A disassembled zinc-carbon battery was shown in Figure 3 and its diverse parts werelisted in Table2.An important part from those parts was zinc casing**,**and it was tested by spectrometer (after cleaning) to find its chemical composition**.**

Figure 2. The spent zinc-carbon batteries.

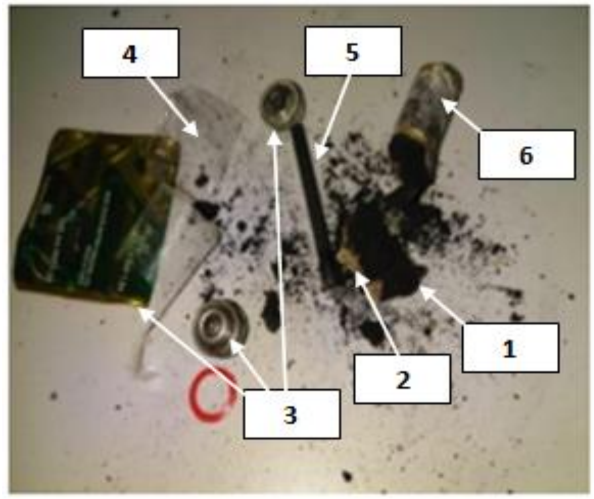

Figure 3. A dismantled AA type zinc carbon dry cell battery

Table2. The zinc-carbon batteries components.

NO.	Material
1	Electrolyte paste
2	Cardboard
3	Steel covers
4	Plastic separator
5	Carbon electrode
6	Anode zinc (zinc casing)

2.2. Reaction Solution

The reaction solution was sulfuric acid (H_2SO_4), it's colorless, concentration of 99% purity and 99.09 g/mole molecular weight, it was used in leaching solution. The sulfuric acid was mitigated by distilled water. The zinc metal parts (zinc casing) were added gradually to the beaker of reaction solution, to prevent the getting out of gases and intoxication with them.

2.3. Laboratory Tools and Instruments

In this work, it was used many simple laboratory tools and instruments. The tools as beakers, pipits, funnel, filtration paper, gloves, glasses, conical flasks. The instruments as sensitive balance, hot plate, drying oven, hood.

2.4 Production of Zinc Sulfate

The experimental parameters to prepare zinc sulfates solution were shown in table3. The aqueous zinc sulfate solution was manufactured by leaching process (selective corrosion). This solution was filtrated to be pure from unwanted substances, the pure solution was putted on the hot plate to remove excess water with evaporation method, the evaporation temperature and heating period were clarified in table3.

The Zinc sulfate was produced synthetically by leaching reaction (selective corrosion) of zinc metal parts with aqueous sulfuric acid as clarified in figure4 and equation(1) summarized the occurred chemical reaction [4].

$$Zn + H2SO4 + 7H2O \rightarrow ZnSO4.7H2O + \uparrow H2 \quad (1)$$

Figure 4. Immersed zinc shell of batteries in sulfuric acid.

Table 3. Experimental parameters to prepare zinc sulfates.

Parameter	Value
Sulfuric Acid Concentration(wt/wt)	10%
Leaching Period (hr.)	24
Evaporation Temperature (C°)	100
Evaporation Period (mn.)	25

3. Results and Discussion

3.1. Chemical Composition of Zinc Casing

The chemical composition test of zinc casing by spectrometer shows that casing includes 99.409 Wt% zinc and very small of lead content and another traces metals, as shown in table 4.

Table 4. Chemical composition of the spent AA type battery anode.

Elements	Pb	Ca	Al	Si	Zn
Wt%	0.386	0.065	0.088	0.052	Rem.

3.2. The resulting Sulfate and Their Shape

It is known that the chemical equation that control the leaching process have two parts, an oxidation reaction and a reduction reaction, to get a solution from that process. The solution of zinc sulfate is the solution resulting from leaching process, which is a result of the ionic decomposition of the zinc metal (Zn ++) of the shell alloy due to its corrosion with sulfuric acid solution, where the divalent zinc metal gives two electrons, it is an oxidation reaction as shown in equation (2).

$$Zn \longrightarrow Zn + 2 + 2e - \quad (2)$$

These two electrons are used by the two hydrogen ions in the sulfuric acid molecule. The sulfuric acid molecule decomposes into the sulfate ion ($SO4^{-2}$) during the corrosion (leaching) process, which has a negative divalent and two hydrogen ion ($2H^{+}$), and each ion is positive monovalent, and that is a reduction reaction as shown in equation (3).

$$H_2SO^4 \longrightarrow SO4 - 2 + 2H - \quad (3)$$

Thus, the positive zinc metal ions unite with the negative sulfate ions to shape zinc sulfate as the aqueous solution form, in addition to the formation of the hydrogen gas molecule by gaining the positive hydrogen ions of the electrons resulting from the decomposition of the zinc metal.

This is stated in equation (1) and it is made up of an oxidation reaction and a reduction reaction.

$$Zn + H2SO4 + 7H2O \rightarrow ZnSO4.7H2O + \uparrow H2 \quad (1)$$

The result solution was filtrated. Aqueous zinc sulfate was gained as shown in figure 5, after the filtered solution was heated to 120C° for a period of 20 minutes (evaporation process). The zinc sulfate resulted was white hydrate substance as a paste shape, as shown in figure 6. This appearance was identical with research results of (Priyanka and others)[5].The zinc sulfate was cannot be gained in a dry powder shape, even if it has been dried for long hours, it is hydrolysed instantly after being removed from the drying oven. This is because of its molecules have a high affinity to merge with the water vapor molecules present in the atmosphere. Therefore, zinc sulfate cannot be gained as a dry powder [5].

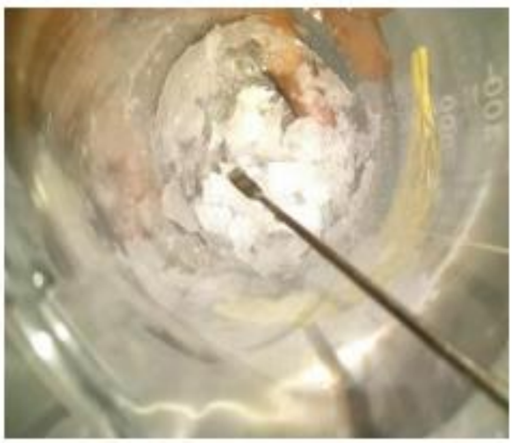

Figure 5. Shape of zinc sulfate after filtration and evaporation.

Figure 6. Shape and colour of resulted zinc sulfate.

3.3. XRD test results for zinc sulfate

The X-ray diffraction (XRD) pattern of zinc sulfate shows in Figure 7, in which four major peaks happened at (2Θ) :19°, 27.5°, 29° and 36°.

The most intense peak for zinc heptahydrate happened at 27.5°. It was noticed by XRD test, zinc sulfate paste to be highly concentrated. These significant rates of zinc sulfate heptahydrate, are congruent to the standard models. The vacillation of the pattern is due to the water molecules that exist in the zinc sulfate heptahydrate.

This clarifies why the resulting zinc sulfate is not stable in a dry or solid form. Whereas, zinc sulfate heptahydrate consists of seven water molecules, so zinc sulfate heptahydrate has the property of being solidly unstable in the natural state.This is consistent with the conclusions of the researcher Zhiwei Xu [13].

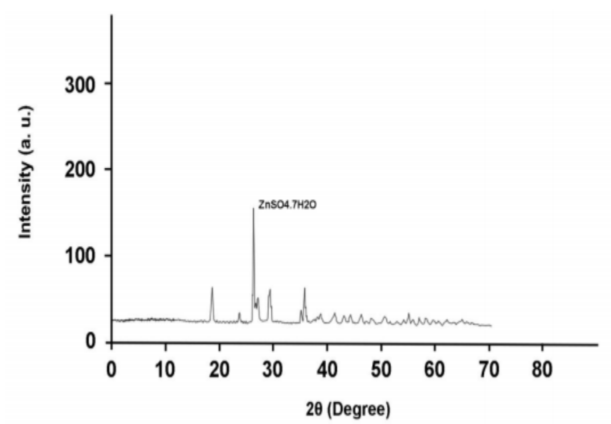

Figure 7. XRD pattern of the zinc sulfate heptahydrate.

4. Conclusions

There is a lot of information inferred from this work:

1. The spent batteries consisted of many engineering materials.
2. Zinc metal occupied of a large amount of spent batteries parts.
3. The purity of zinc anode (zinc alloy) is more than 99%.

4. The reaction in the leaching process (selective corrosion) is non-exothermic and continuous at room temperature but creates hydrogen gas by-product.
5. The product is ($ZnSO_4 \cdot 7H_2O$), as shown in the XRD test diagram. Which is used in the production of food supplements.

6. The product is white in color and not in stable dehydration state. i.e., the hydration state associated with zincsulfate, so that anhydrous zinc sulfate is not found naturally. Therefore zinc sulfate heptahydrate has a paste form.

Conflict of interest

The authors declare no conflict of interest in publication of this research.

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