

LEACHING OF METALS FROM SPENT BUTTON AND COIN CELLS

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ABSTRACT

As a result of accelerated technical and technological development, electronic waste has become a prime environmental threat for its high amount and toxicity. Recently the request for portable devices has increased fiercely such as smart watches, insulin pumps, remote controls etc. Therefore, to power up these portable devices, a particular battery known as button and coin cells are widely used nowadays. These cells are made of heavy metals which are highly toxic at low concentrations, also they cannot be degraded or destroyed.

This study focuses on recovering heavy metals from spent button cells and dissolution of spent button cells as a whole contrasting with other studies performed where crushing or manual dismantle were applied. Different acids were tried (Hydrochloric acid, nitric acid, and sulfuric with different concentrations). The search for ideal dissolution conditions was performed by examining different variables: acid molarity, temperature, time and solid/liquid ratio on both alkaline and silver button batteries separately. Results revealed that the ideal conditions are as follows: 7.0 M HNO₃, 30 °C, 30 mins, and 2:50 S/L ratio of spent batteries.

Keywords: Spent Button cells, dissolution, nitric acid, heavy metals, hydrometallurgy, urban mining.

INTRODUCTION

Municipal Solid Waste (MSW) management has become a major problem especially in developing countries because of scarcity of funds, efficient urban plans, tools for waste collections, firm laws besides rapid increase in population. Goods and wastes at the end of their

life (EoL) must be either properly disposed or processed for further recycling and/or producing energy to avoid negative impacts on marine and earth pollution (Moyen Massa and Archodoulaki, 2023)

According to Waste and Sustainable Development Goals (2016), there are more than 7 billion people on the planet producing waste every day. A staggering half of that waste is not collected, treated or safely disposed, and it is causing a global waste crisis. The Sustainable Development Goals (SDGs) cannot be achieved except if waste management is dealt with as a top priority (El Masry, 2019).

UN's sustainable development goal #12 focuses on promotion of sustainable consumption of waste electrical and electronic equipment (WEEE) through specific policies and international agreements on the safe management of toxic wastes to the environment. (WEEE) contains hazardous that can possibly harm individuals and environment if mismanaged. For example, combustion activities responsible for emitting toxic gasses in the atmosphere causing pollution, additionally landfill leachates can carry poisonous elements to groundwater. In most developing countries safe collection of e-wastes doesn't meet the demands or reflect the concept of sustainable development (Ali and Shirazi, 2023).

E-waste as computers, mobile phones, televisions, batteries and irons etc., contains metals, classified into precious metals PMs (Au and Ag), platinum group metals PGM (Pd, Pt, Rh, Ir and Ru), base metals BMs (Cu,Al, Ni,Sn,Zn and Fe), metals of concern MCs (Hg, Be, In, Pb, Cd, As and Sb) and scarce elements SEs (Te,Ga, Se, Ta and Ge) (Hagelucken, 2006).

E-waste contains pollutants like batteries and capacitors considered as hazardous waste (a waste that poses substantial or potential threats to public health or the environment, ignitable,

corrosive, reactive or/and toxic). These components are present in small quantities, around 2% of the total weight of e-waste, but as they contain high level of stable pollutants such as heavy metals which are toxic or poisonous even at low concentrations, they cannot be degraded nor destroyed. Therefore, elimination and recovery of toxic and/or precious metals from industrial waste is an absolute necessity. Furthermore, hazardous waste is a special type of waste because it cannot be disposed of by common means like other by-products of our everyday lives (Vyas, 2010).

Urban Mining is the “integral management of the anthropogenic stock with the aim to recover raw materials from long-living products, buildings, infrastructure and tailings. Some definitions also consider the energetic use of discarded products through incineration. Urban Mining attempts to manage not only the waste of today but also anticipate and capture the value contained in the waste of tomorrow. Urban mining attempts to manage not only metals, but the idea is largely applied to other anthropogenic materials such as woods, stones, infrastructure, and industrial minerals (Cossu, 2013).

(Tercero *et al.*, 2020) showed that both conventional mining and urban mining share the principle of exhaustible sources of raw materials and urban mining is no absolute avoidance of raw materials depletion. Yet urban mining induces additional circularity and extends the availability of known and yet to be known geological deposits. The discarded specialty batteries containing valuable metals are excellent resources in the context of urban mining.

Portable devices have experienced a dramatic growth in number such as cellular phones, portable computers, toys, radios and cordless power tools. However, this growth would have been impossible without the introduction of new batteries with improved performance which explains

why batteries are widely used nowadays shifting towards miniaturization leading to the broad usage of specialty cell batteries because of their lightweight, operating longevity, minimized expense, versatility, high capacity per unit mass (Pistoia, 2005). Button and coin batteries are classified into four common types, in this work we'll focus on leaching metals from both Alkaline Zinc/manganese and Silver Oxide batteries abbreviated as LR and SR respectively. (Linden and Reddy, 2002).

This study aims to develop an effective hydrometallurgical route for metal recovery from spent button and coin cells and dissolution of spent button and coin cells as a whole contrasting with other studies performed where crushing or manual dismantle were applied.

MATERIALS AND METHODS

Materials: Spent button and coin batteries (SBCs) of different manufacturers, sizes and compositions were collected from several local watch repairing shops in Cairo, Egypt. They were sorted accordingly with respect to their chemistries to SR and LR batteries. The weight of each type is determined using a digital balance. Leaching trials were done using different acids 69% Nitric acid (Alpha chemika), 37% hydrochloric acid (Adwic), 94% sulphuric acid, 30% hydrogen peroxide (El-Nasr company for Pharmaceuticals and Chemicals), deionized water. Chemicals used in this study were of analytical grade and used without further purification. The practical work was divided into two parts, first the leaching process, and second the selective precipitation of metals.

Part one: Battery dissolution: Unlike other studies, spent batteries were neither crushed nor manually dismantled, however the whole battery was dissolved in different concentrations of

acids such as hydrochloric acid, sulphuric acid and nitric acid separately in addition to hydrogen peroxide as an oxidizing agent to achieve maximum dissolution results.

The establishment of optimal dissolution parameters was executed by examining the following variables: molarity of acid, Solid/liquid (S/L) ratio, temperature and time. However hydrochloric and sulphuric acids used showed no promising results, only diluted nitric acid results were significant.

Different concentrations of nitric acid were prepared of 4M, 5M, 6M, 7M and 8M. For each trial 50 ml of various nitric acid solution was used to dissolve a known weight of SBCs.

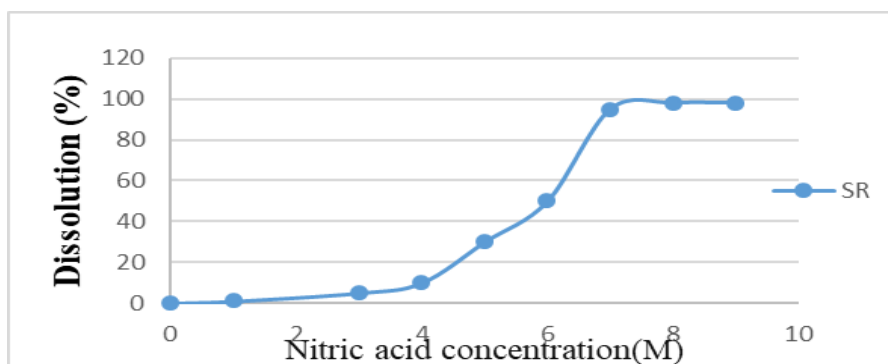
Solid/Liquid ratio experiments were performed after determining the ideal molarity for dissolution on 2, 4, 6 and 9 grams using 10ml of 7 M nitric acid.

The effect of time was monitored for each experiment. The temperature varied from room temperature 25 to 60 Celsius to examine the effect of temperature on battery dissolution under magnetic stirring. The previous trials were carried out on both silver oxide (SR) and alkaline (LR) batteries separately. The solutions were filtered and collected in two jars after each trial. After filtration of each precipitate, the solutions were analyzed by ICP-OES spectrometry to determine the metals present in Table (1) as stated in the study of (Quintanilha *et al.*, 2014).

Part two: Selective precipitation: After identification of the metals in the solution, many trials were done to selectively precipitate the desired metal by adjusting the pH and using different reagents as displayed in the general flowchart Scheme.1

RESULTS AND DISCUSSION

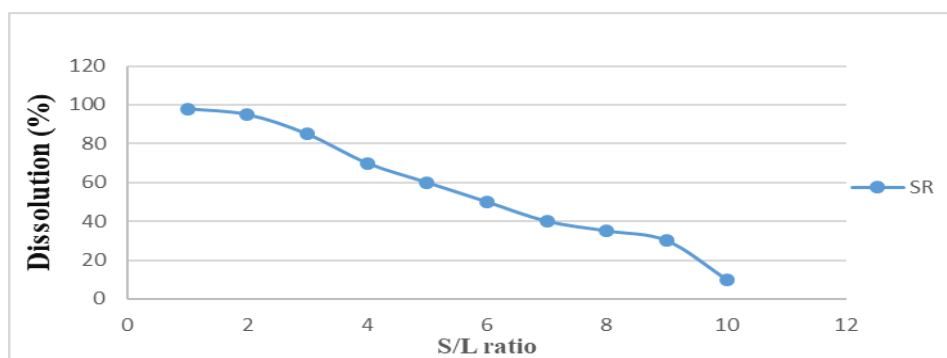
1- Effect of Nitric acid concentration: The most challenging part in the practical work is to dissolve the battery without using heavy concentrated chemicals that cause hazardous fumes to humans and environment, also without losing any parts of the battery during the manual dismantling step. Moreover, manual dismantling a miniature battery is tedious, requires a lot of effort and handy skills also wastes time when working on a broad scale. Sulphuric and hydrochloric acids reacted with the stainless-steel case turning the solution into green color due to presence of iron in the case while showing no promising results in dissolving the battery completely. These conditions were achieved by preparing the optimal conditions for almost complete dissolution of the spent batteries by using diluted nitric acid, where both SR and LR batteries exhibit the same dissolution behavior. Fig.2 shows that battery dissolution increased with an increased molarity of nitric acid, at 7M and higher molarities almost 99% dissolution were fulfilled except for the gasket, separator and carbon residues.



Figure(2): Effect of nitric acid concentration on silver oxide batteries dissolution percentage.

2- **Effect of Solid/Liquid ratio:** To determine the effect of Solid to liquid ratio more accurately, different battery weights in different acid concentrations were studied. Fig.3 displays the effect of S/L ratio on dissolution, where the lowest amount of solid (2 gm) exhibits the highest dissolution percentage. Dissolution decreases gradually with higher sample weights because the amount of nitric acid was not sufficient to dissolve all the solid present. However, upon increasing the liquid volume, higher dissolutions were observed. The previous study of (Aktas, 2010) stated that 5ml of diluted nitric acid was enough to dissolve 50 mg of cell powder after the manual dismantling, where the dissolution decreased with the increase of the cell powder. Also, Provazi *et al.*, (2011) used solid/liquid ratio ($S/L = 1/10 \text{ g mL}^{-1}$) to prepare the solution for metals recovery which is a bit lower than the presented work due to the grinding step of the whole battery before the leaching process.

The recent study of Norouzi *et al.*, (2020) used 2M of nitric acid as a solvent with an S/L ratio 2% (2g solids/100 ml solution) also in agreement with the current study taking into consideration the dismantling step before leaching.



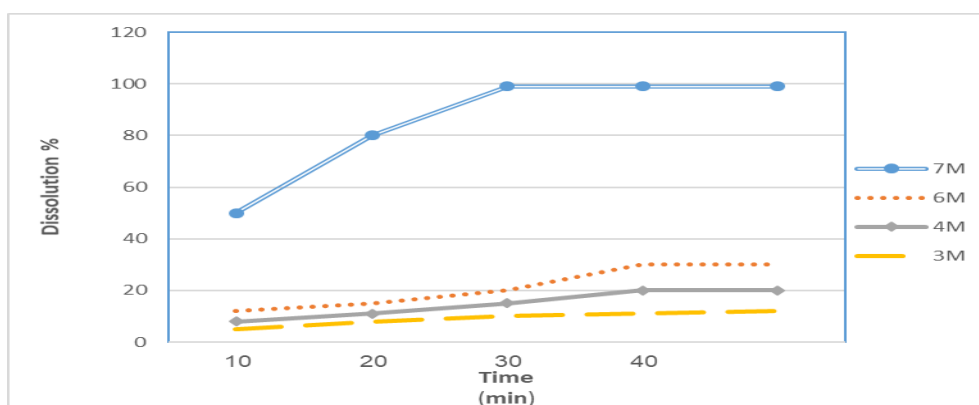
Figure(3): Effect of Solid/liquid (S/L) ratio on dissolution (7M, 50ml HNO₃, 2gm spent battery at 25 °C, 150 rpm).

3- Effect of Time : The pattern of dissolution at different time intervals was shown in Fig.4

Different nitric acid concentrations were experimented, only 7M showed promising results. For instance, dissolution of 45% of the battery was observed after 10 min in 7M HNO₃ solution. However, under the same conditions, extending the time to 15 min can achieve up to 65% dissolution.

Dissolution of 80% was observed after 20 min using 7M HNO₃, nevertheless 99% was achieved after extending the time to 30 min. No further significant results were noted after 30 minutes.

Jadhav and Hocheng, (2013) study revealed 45% dissolution of silver after one hour, however when the time extended to 3 hours 98% was achieved. While interestingly in this study, a higher leaching of metals was detected as the shaking speed increased and significant less time was recorded when magnetic stirring was applied on all parameters, 150 rpm was found to be the ideal.

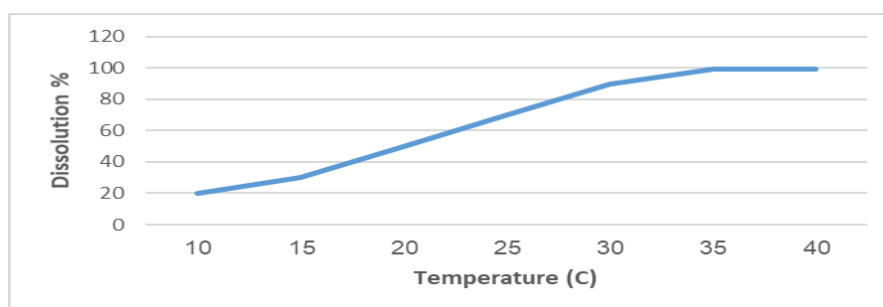


Figure(4): Effect of time on dissolution with different HNO₃ concentrations at room temperature.

4- **Effect of Temperature:** Temperature influenced the dissolution process as depicted in **Fig.5**. Studies were carried out at varying temperatures from 25 to 35 °C. At lower temperature and concentration 25 °C and 5M HNO₃ solution, dissolution of 30% was obtained, whereas at 35 °C, dissolution of 95% was observed. The dissolution distinctly increased with the increasing temperature. Clearly a different behavior of dissolution appeared when 7M HNO₃ solution was

used, the battery was entirely dissolved at 35 °C. However, carrying out the trials in room temperature with extended time and continuous magnetic stirring resulted in complete dissolution.

Thus temperatures of 40 and 50 °C were not investigated. According to these results, it's obvious that increased temperatures yields higher dissolution effectiveness. The results of present study are favorable and has less impact on the environment as compared to those of Judhav *et al.*, (2018) that achieved 100 % leaching efficiency at 60 °C, at lower temperatures (30 °C) only 80 and 41 % leaching of Zn and Ag respectively.

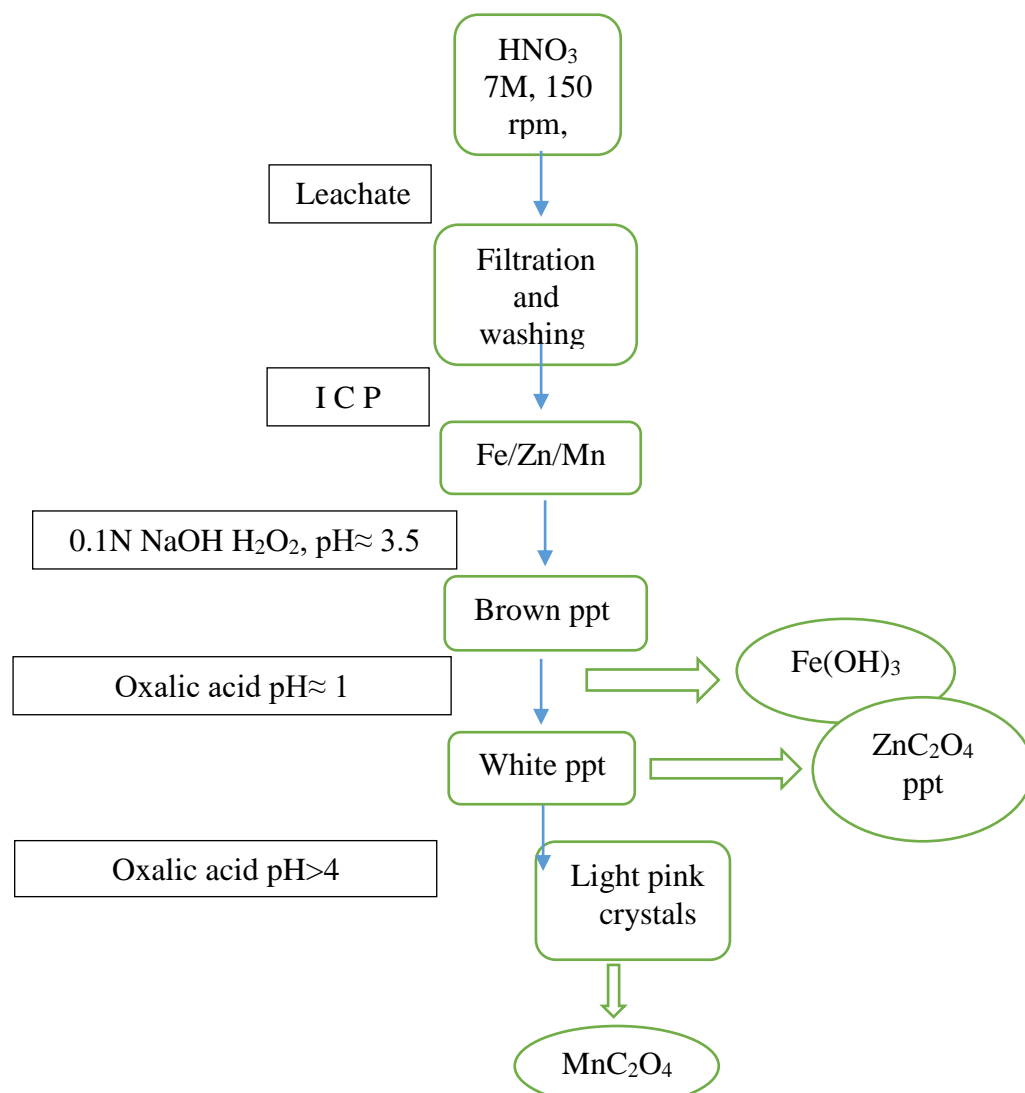


Figure(5): Effect of temperature on dissolution efficiency in 7 M nitric acid solution concentration.

Table 1: Metallic ions in the leachates obtained by ICP/OES. spectrometry
Selective precipitation

Batter y type	Ag g/L	Fe g/L	Zn g/L	Cr mg/L	Ni mg/L	Mn g/L
LR	-	27.5	4.6	-	-	4.1
SR	6.5	20.40	4.10	6.0	900.0	-

Selective precipitation



Scheme(1): A general flowchart shows how metals in alkaline zinc/manganese battery were selectively precipitated.

CONCLUSION

Depending on the findings of the current study, the optimum dissolution conditions are as follows:

- 7 M nitric acid was verified to be enough to dissolve almost 90% of the button cell excluding the gasket, separator and the carbon in the stainless steel cap, nitric acid concentration was maintained constant during the leaching process. Also it was enough to work at room temperature to save energy.

Using S/L ratio as 2/50 ml of spent cells in a 30 °C temperature soaked for 30 minutes' maximum.

- Only nitric acid can be used in the dissolution process.
- The metal content in the aqueous phase was determined using ICP spectrometry and most of the metals were successfully recovered.
- The process has proven to be easy and straightforward.

REFERENCES

- Aktas, S. (2010). Silver recovery from spent silver oxide button cells. *Hydrometallurgy*, 104(1): 106-111.
- Ali, S., and Shirazi, F. (2023). The Paradigm of Circular Economy and an Effective Electronic Waste Management. *Sustainability*, 15(3): 1998.
- Cossu, R. (2013). The Urban Mining concept. *Waste management*, 33(3): 497-500.
- El Masry, R. (2019). Good governance and integration for sustainable municipal solid waste management: a case study of Egypt. [Master's Thesis, the American University in Cairo]. AUC Knowledge Fountain. <https://fount.aucegypt.edu/etds/805>

- Hagelucken, C. (2006). Improving metal returns and eco-efficiency in electronics recycling-a holistic approach for interface optimisation between pre-processing and integrated metals smelting and refining. In Proceedings of the 2006 IEEE International Symposium on Electronics and the Environment, 2006. (pp. 218-223). IEEE.
- Linden, D., and Reddy, T. B. (2002). Lithium batteries (Vol. 3). McGraw-Hill.
- Jadhav, U., and Hocheng, H. (2013). Extraction of silver from spent silver oxide–zinc button cells by using *Acidithiobacillus ferrooxidans* culture supernatant. *Journal of cleaner production*, 44: 39-44.
- Jadhav, U., Su, C. H., Chakankar, M., and Hocheng, H. (2018). Leaching of metals from waste silver oxide-zinc button cell batteries by *Aspergillus niger*. *Batteries*, 4(4): 51.
- Moyen Massa, G., and Archodoulaki, V. M. (2023). Electrical and Electronic Waste Management Problems in Africa: Deficits and Solution Approach. *Environments*, 10(3): 44.
- Norouzi, A., Adeli, M., and Zakeri, A. (2020). An innovative hydrometallurgical process for the production of silver nanoparticles from spent silver oxide button cells. *Separation and Purification Technology*, 248: 117015.
- Pistoia, G. (2005). Batteries for portable devices. 1st Edition, pp: 33-41.
- Provazi, K., Campos, B. A., Espinosa, D. C. R., and Tenório, J. A. S. (2011). Metal separation from mixed types of batteries using selective precipitation and liquid–liquid extraction techniques. *Waste Management*, 31(1): 59-64.
- Quintanilha, C. L., Afonso, J. C., Vianna, C. A., Gante, V., and Mantovano, J. L. (2014). Recovery of manganese and zinc via sequential precipitation from spent zinc–MnO₂ dry cells after fusion with potassium hydrogensulfate. *Journal of Power Sources*, 248: 596-603.
- Tercero, L., Rostek, L., Loibl, A., and Stijepic, D. (2020). The Promise and Limits of Urban Mining. Fraunhofer Institute for Systems and Innovation Research ISI.
- Vyas, S. (2010). Solid Waste Management–A Step towards Sustainable Development. *Asia Pacific Business Review*, 6(1): 122-127.

استخلاص المعادن من البطاريات العملة و الزرار المستعملة

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المستخلص

نظرا للتطور التقني و التكنولوجي و التقني المتسارع، اصبحت النفايات الالكترونيه تهديدا بيئيا رئيسيه نتجه لكميتها العاليه و سميتها. في الاونه الاخيره، ازداد الطلب علي الاجهزه المحموله بشده مثل الساعات الذكيه ومضخات الانسولين و اجهزه التحكم عن بعد و ما الي ذلك. ولتشغيل هذه الاجهزه المحموله يستخدم حاليا بطاريات تعرف باسم البطاريه الزرار او بطاريه العملة. هذه البطاريات تحتوي علي معادن ثقيه بكميات صغيره ولكن لا يمكن تحللها او التخلص منها. تهدف هذه الدراسه علي التركيز علي ذوبان البطاريه العملة و الزرار ككل علي عكس الدراسات الاخري التي تعتمد علي تكسير البطاريه او التفكيك اليدوي. تمت تجربه احماض مختلفه (حمض النيتريك، حمض الهيدروكلوريك، حمض الكبريتيك) بتركيزات متعدده. تم فحص متغيرات مختلفه مثل تركيز حمض النيتريك، درجه حراره، الوقت و نسبه ماده الصلبه للماده السائله لكل من نوعين البطاريات المدروسه.

بناءا علي نتائج التجارب في الدراسه الحاليه، فان الظروف المثاليه للذوبان الكامل هي:

- 50 مللي من ٧ مولار حمض نيتريك.
 - ٣٠ درجه حراره مؤويه
 - ٣٠ دقيقه ل ٢ جرام من البطاريات المستهلكه.
- الكلمات الداله: بطاريات الزرار المستهلكه، الذوبان، حمض النيتريك، فلزات ثقيه، التعدين الحضري.