

Recovery of Vanadium and Lanthanides from the Processed Carbonate-Rich Latosol of Abu Thor Locality, Southwestern Sinai, Egypt

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Abstract

In a previous work, chemical processing of carbonate-rich latosol of Abu Thor locality have successfully recovered both of U and Cu contents by applying two successive steps of leaching processes. From the latter, the remaining two metal values; namely V and Lns were left behind in the spent residue. The latter represents the feed material of the present work for V (1050 ppm) and Lns (649 ppm) recovery.

The work involves selective leaching process for V using alkali breakdown with Sodium hydroxide (NaOH) followed by its precipitation as V_2O_5 . The Lanthanides (Lns) left behind was then leached by using sulfuric acid followed by its precipitation as a highly pure Lns oxalate.

Key Words: Recovery, vanadium, lanthanides, sulfuric acid, sodium hydroxide.

1. Introduction

Abu Thor locality of west central Sinai area is an example of the radioactive anomalies that are associated with carbonate- rich latosol which have been mainly derived from the Lower Carboniferous siltstone, clays, shales of the middle dolomitic -limestone series of Um Bogma Formation (ElAassy et al. ,1886). These authors concluded that the latosol at both Allouga and Abu Thor localities are of good uranium potentiality in which some secondary uranium minerals together with some other minerals of Cu, V, and Lns are visible besides the famous Fe-Mn deposits in different concentrations.

Generally, vanadium could actually be leached from its ores by either acidic or alkaline (NaOH or Na_2CO_3) breakdown as well as salt roasting with NaCl (fluxing). The produced pentavalent vanadium salt undergoes H_2O leaching to dissolve its vanadium content. The solvent extraction or ion exchange and direct precipitation techniques were applied for the recovery of vanadium from the prepared leach liquor. Vanadium is expected to be in the

form of $\text{VO}_3(\text{OH})_2$ and VO_4^{-3} (Greenwood, et al., 1984). Fig.(1) represents the general flowsheet for chemical processing of vanadium from the major vanadium- bearing materials, (Eatough et al., 1984). On the other hand, direct acid leaching has been used in commercial leaching procedures. Haoran et al. (2008) used acidic leaching with H_2SO_4 to extract V from vanadium bearing-clay mineral. The leached vanadium was then precipitated with NH_4Cl after removing the associated impurities via their precipitation with NaOH . According to Zhang et al. (2011) the salt roasting leaching process was devised to extract V from the oxidized carnotite ore in the thirties of the last Century. It was applied to produce water soluble V products and to separate between V and U. The salt roasting process was performed by mixing the ground ore (-10 mesh size) with 6-10 % of NaCl and roasting the mixture at a temperature ranging from 825 to 850°C for 1 to 2 h in a multiple roaster. The calcined material was then cooled rapidly and leached with H_2O to extract the water soluble sodium vanadate. The remained residue was further treated with dilute acid to dissolve its U content and additional acid-soluble V compounds, (Holloway and Etsell, 2002).

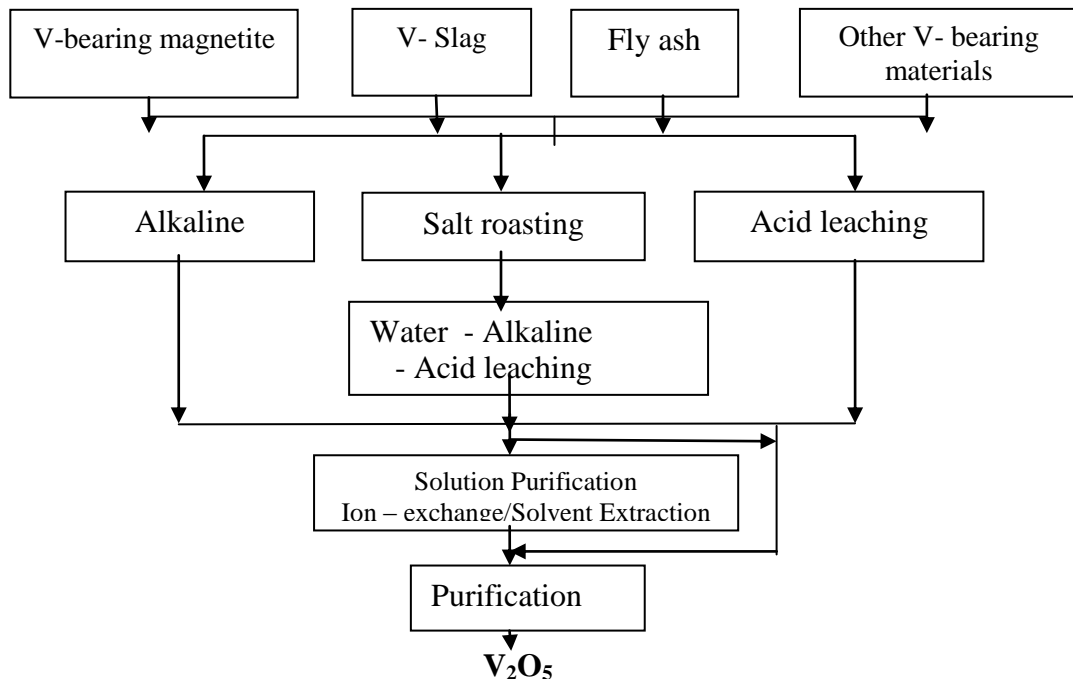


Fig. (1): Represents the general flowsheet for chemical processing of vanadium from the major vanadium- bearing materials

With respect to Lns recovery, several methods that industrially be applied have been studied for the breakdown of the most common lanthanides minerals via acidic or alkaline breakdown. The sulfuric acid method has been depending on the acid/ore ratio, temperature and concentration. On the other hand, alkali breakdownacid baking with sulfuric acid is a very common process. The powdered ore is mixed with concentrated sulfuric acid and baked at temperatures between 200 and 400 °C for several hours. The resulting cake is leached with water to dissolve Lns as sulfates. The lanthanides recovery based on lanthanides double sulfates precipitation or Lns oxalates, (Marczenko, 1976).

In the present work , the starting feed material is the spend residue obtained after applying two successive leaching processes for selective recovery of U and Cu from the original raw material of carbonate-rich latosol occurring at Abu Thor locality of Southwestern Sinai mineralization, (El-Sheikh et al. , 2015). Selective uranium leaching was achieved by using urea while copper was subsequently and relatively leached with mixed solutions of ammonium hydroxide and ammonium carbonate. The optimum leaching conditions for uranium include urea solutions of 60g/L concentration at room temperature. for 90 min. in a S/L ratio of 1/5. The uranium leaching efficiency was found to attain up to 97.5%. The uranium leached ore sample was then subjected to almost complete Cu dissolution (98.9%) using the optimum condition of 120 g/L ammonia solution and 35 g/L ammonium carbonate for 2 hours and in a S/L ratio of 1/5 in (El-Sheikh et al. ,2015). The remaining two metal values; namely V and Lns which were left behind in the spent residue were found to assay 1050 and 649 ppm respectively. So, the present work was directed to study the recovery of both V and Lns metal values from the spent residual material. These involved V recovery by alkaline leaching followed by classical acidic leaching procedures for Lns.

2. Materials and Methods

2.1. Materials

As previously mentioned, the starting feed material of the present work is the spend residue obtained after applying two successive leaching processes for selective recovery of U and Cu from the original raw material of carbonate-rich latosol of Abu Thor locality at Southwestern Sinai **El-Sheikh et al., Op. cited.** This dried residue was subjected to

two successive recovery procedures for V and Lns. The applied successive leaching procedures include, alkali breakdown of vanadium followed by classical acidic leaching for Lns.

2.2. Methods

2.2.1. Alkali breakdown of vanadium

For alkali breakdown of vanadium several leaching experiments have actually been performed including fusion with NaOH to optimize the relevant dissolution factors. In these experiments, a suitable weight of the working spent ore residue was mixed with a suitable weight of NaOH in a porcelain crucible for different time periods and different temperatures. The obtained melt was then cooled and washed with distilled water, filtered and made up to a volume. The interesting metal values were then analyzed in the filtrate to calculate the dissolution efficiency percent.

2.2.2. Acidic leaching of lanthanides

Several acidic leaching experiments were performed for recovering Lanthanides from the spent ore residue free from vanadium by using sulfuric acid. Factors controlling leaching process such as; acid concentrations, effect of temperature and effect of S/L ratio have been studied. At the end of each leaching experiment, the obtained aliquot filtrate were analyzed for Lns to calculate their leaching efficiency.

2.2.3. Analytical procedures

The content of the processed metal values (V and Lns) whether in the spent ore residue or in the different stream solutions obtained during leaching and recovery steps were determined by proper techniques. Thus, Lns were spectrophotometrically determined by the chromogenic reagent Arsenazo-III (**Merczenko, 1986**) while vanadium was analysed by using atomic absorption spectrophotometry (AAS) model Unicam 969, England.

Finally, to insure the purity of the obtained metal concentrates the environmental scanning electron microscope (ESEM) together with chemical analyses were used.

3. Results and Discussion

3.1. Recovery of vanadium and Lns

Chemical composition (Table 1) of the original carbonate-rich latosol ore material of Abu Thor locality reflects the carbonaceous nature of the raw material. From the latter, and after the recovery of U and Cu, the dried residue was then subjected to two successive

recovery procedures for V and Lns .Theapplied successive leaching procedures include, alkali breakdown of vanadium followed by classical acidic leaching for Lns.

Table (1): Chemical composition of the originalatosol technological raw ore sample(After El- Sheikh et al. ,2015).

Component	wt.%	Component	wt.%
SiO ₂	12.5	K ₂ O	0.42
TiO ₂	0.13	P ₂ O ₅	0.03
Al ₂ O ₃	5.84	SO ₄	2.07
Fe ₂ O ₃	4.65	*L.O.I .	34.90
MnO	3.33	CuO	9.65
MgO	3.00	Cl	0.70
CaO	24.73	Total	100.7
Na ₂ O	0.04		
Trace element	ppm	Trace element	ppm
Ba	1311	Pb	159
V	789	Cr	190
Ni	100	Sr	801
Nb	34	Ga	40
Zn	325	Zr	330
Rb	102	U	700
Cd	13	Co	24
Y	200	∑ Lns	456

*L.O.I. = loss on ignition at 1000°C

3. 1.1 Recovery of vanadium

Recovery of V from the study ore residue include two steps namely; alkali breakdown by using sodium hydroxide followed by vanadium precipitation.

3. 1.1.1 Alkali breakdown

In this method, NaOH was mixed with the spent ore residue in different weight ratios and then allowed for heating at different temperatures for different times. After cooling, the fused cake was then dissolved in distilled water for 30 min. to bring out the vanadium content in solutions to determine the dissolution efficiency.

i- Effect of spent ore residue /NaOH reagentratio (S/R):

To study the effect of spent ore residue / NaOH ratio upon the dissolution efficiency of V, a set of experiments were performed using ratios ranging from 1:1 to 1:5, while the other fusion conditions were fixed at 200 °C for 3 h. The obtained results are given in Table (2).

Table (2): Effect of Ore/ NaOH ratio upon vanadium dissolution efficiency.

Spent ore residue/NaOH ratio	V Dissolution Efficiency, %
1/1	80.18
1/2	86.36
1/3	98.79
1/4	98.86
1/5	98.82

From this table, it can be concluded that the dissolution efficiency of vanadium increases with decreasing the spent residue / NaOHratio , this indicating its effective role on the ore breakdown. Thus, by decreasing the spent residue / NaOH ratio from 1/1 to 1/3 the corresponding dissolution efficiencies increase from 80.2 to 98.8 %. Beyond 1/3 spent oreressidue / NaOHratio, only a very slight steady increase in the dissolution efficiencies of vanadium has been achieved. Accordingly, spent ore residue / NaOH ratioof 1/3 would be considered as optimum at which the leaching efficiency of vanadium attained 98.8%.

ii- Effect of fusion temperature:

The effect of fusion temperature upon the dissolution efficiencies of vandium from spent ore residue, was studied in the range of 120 to 300 °C. Other fusion conditions were fixed at spent ore residue / NaOH ratio of 1:3 and fusion time of 3 h. The obtained results ,table(3) indicate that fusion temperature is the most important factor for spent ore residue breakdown. However, increasing the fusion temperature from 120 to 200°C has a significant increase in V dissolution efficiency from 58.3 to 98.8 %. While at fusion temperature of 250 and 300 °C an adverse effect on the V dissolution efficiency takes place where it decreased to 94.39 and 92.12 % respectively . This may be attributed to dissolution of many undesired impurities from the ore residueor the beginning of V hydrolysis. Thus, 200 °C was considered as the optimum fusion temperature.

Table(3):Effect of fusion temperature upon vanadium dissolution efficiency.

Temp., °C	V Dissolution Efficiency, %
120	58.31
150	94.45
200	98.79
250	94.39
300	92.12

iii- Effect of fusion time:

The effect of fusion time upon the dissolution efficiency of vanadium from the spent ore residue was studied in the range of 1 to 5 h. Other fusion conditions were fixed at a spent ore residue / NaOH ratio of 1:3 and fusion temperature of 200 °C. The dissolution efficiency of the vanadium is given in table (4).

Table (4): Effect of fusion time upon vanadium dissolution efficiency .

Time,h.	V Dissolution Efficiency, %
1	55.24
2	61.47
3	98.79
4	85.76
5	61.34

From the obtained results, it is clearly evident that increasing the fusion time from 1 to 3 h increases the dissolution efficiency of vanadium from 55.2 to 98.8%. On the other hand, further increase in the fusion time to 4 and 5 h has adversely affected the dissolution efficiency of vanadium due to the beginning of V hydrolysis.

Finally, from the foregoing results it can be concluded that, using fusion method is more convenient to bring out most of the vanadium content into solution. The obtained

optimum conditions for dissolving 98.8 % of the vanadium from spent ore residue can be summarized as following:

- Fusion time : 3 h.
- Fusion temperature : 200 °C
- Spent ore residue / NaOH ratio : 1/3

3. 1.1.2. Precipitation of vanadium

To prepare a rich V leach liquor, 600 g of spent ore residue was carefully mixed with 1800 g of NaOH and fused for 3 h at 200 °C. The fused cake was then leached with 600 ml distilled water to obtain the dissolved vanadate ions. The obtained vanadate solution may contain small amounts of V^{4+} , which can be quickly oxidized to V^{5+} . This was accomplished by the addition of 30 % H_2O_2 to the prepared solution to oxidize V^{4+} to V^{5+} . The pH of the latter solution was then adjusted to pH 8 by using 30 % H_2SO_4 to precipitate V. The latter precipitate has been subjected to calcinations at 800°C to form V_2O_5 , Fig.(2).

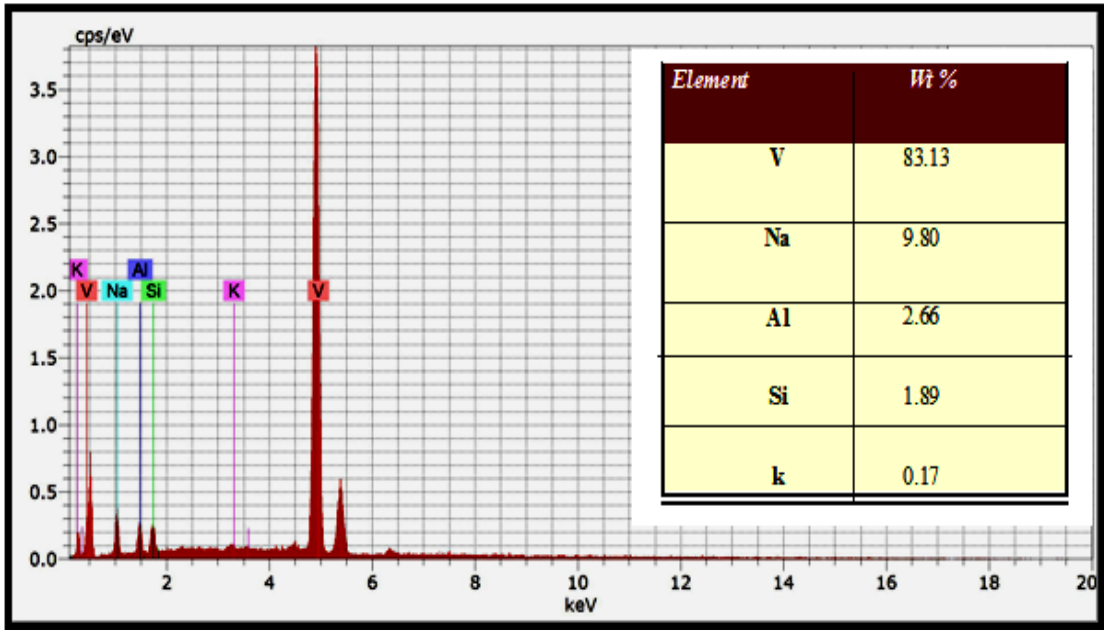


Fig.(2): ESEM- EDX analysis of the prepared V_2O_5 .

3. 1. 2. Recovery of Lns

After removing of vanadium from the spent ore residue, acidic agitation leaching process by using sulfuric acid was performed to dissolve included Lns content.

3. 1. 2.1. Acidic leaching of Lns

To optimize the leaching condition of Lns, the following leaching factors were studied.

i. Effect of H₂SO₄ concentration

The effect of H₂SO₄ acid concentration upon the leaching efficiency of Lns from spent ore residue free from vanadium was studied between 40 and 200 g/L, and the other leaching conditions as contact time (3 h)and solid / liquid ratio(1/3) at room temperature were fixed. The obtained results, Table (5) ,indicated that, the best acid concentration was 80 g/L for leaching about 97% of Lns content. At the high acid concentration of 200 g/L, Lns leaching efficiency was decreased to about 87% due to the formation of Lns double sulfates.

Table (6): Effect of sulfuric acid concentration upon Lns leaching efficiency.

Conc. of sulfuric acid g/L	Lns Leaching efficiency, %
40	65.89
60	79.16
80	97.11
100	96.90
200	87.45

ii. Effect of stirring time:

For studying the effect of stirring time upon Lns leaching efficiency, a series of leaching experiments have been performed by varying the stirring time between 60 and 180 min. The other leaching conditions were fixed at acid conc of 80 g/L, solid / liquid ratio of 1:3, at room temperature. Table (6). From the obtained results, it is noticed that by increasing the stirring time, the leaching efficiency of Lns increases and reaches its maximum value 96.18% at 120 min. Increasing the leaching time to 180 min., there is no marked increase in the leaching efficiency of Lns.

Table (6): Effect of stirring time upon Lns leaching efficiency.

Effect of stirring time, min.	Lns Leaching efficiency, %
60	70.25
80	90.36
120	96.18
150	96.87
180	97.11

iii. Effect of the solid / liquid ratio

To study the effect of S/L ratio upon leaching efficiency of Lns a series of leaching experiments were performed at the solid / liquid ratio (S/L) range of 1:3, 1:4 and 1:5 at the fixed conditions of 80 g/L H₂SO₄, stirring time of 120 min. at room temperature. The obtained results, Table(8) indicated that, at the S/L ratio of 1/3 to 1/5, only slight increase in the leaching efficiencies of Lns takes place. Thus, 1/3 would be considered as the optimum S/L ratio.

Table. (7): Effect of S/L ratio upon Lns leaching efficiency.

Solid /liquid ratio	Lns Leaching efficiency, %
1:3	96.18
1:4	97.08
1:5	97.11

Finally, from the foregoing acidic leaching study, it can be concluded that the optimum leaching conditions for dissolving 96.2% Lns content would be summarized as following:

H₂SO₄ concentration: 80 g/L

Stirring time: 120 min.

Temp.: room

S/L ratio: 1/3

3. 1. 2.2. Precipitation of Lns

To prepare a rich Lns leach liquor, 3000 g of spent ore residue free from V was subjected to sulfuric acid agitation leaching under the obtained leaching conditions. A volume of 9 liter was obtained assaying 208 mg / L Lns. To increase the concentration of

Lns, this leach liquor was then subjected to evaporation process to reduce the volume to 3 liters in order to obtain a Lns- oxalate concentrate . The latter was accomplished by adjusting the pH of the solution to 4.5, then by the addition of 10% oxalic acid ,Lns oxalate was precipitated at pH 1. The obtained Lns oxalate precipitate was then calcined at 800 °C for 3 h and analyzed by using ESEM-EDEX technique Fig.(3).

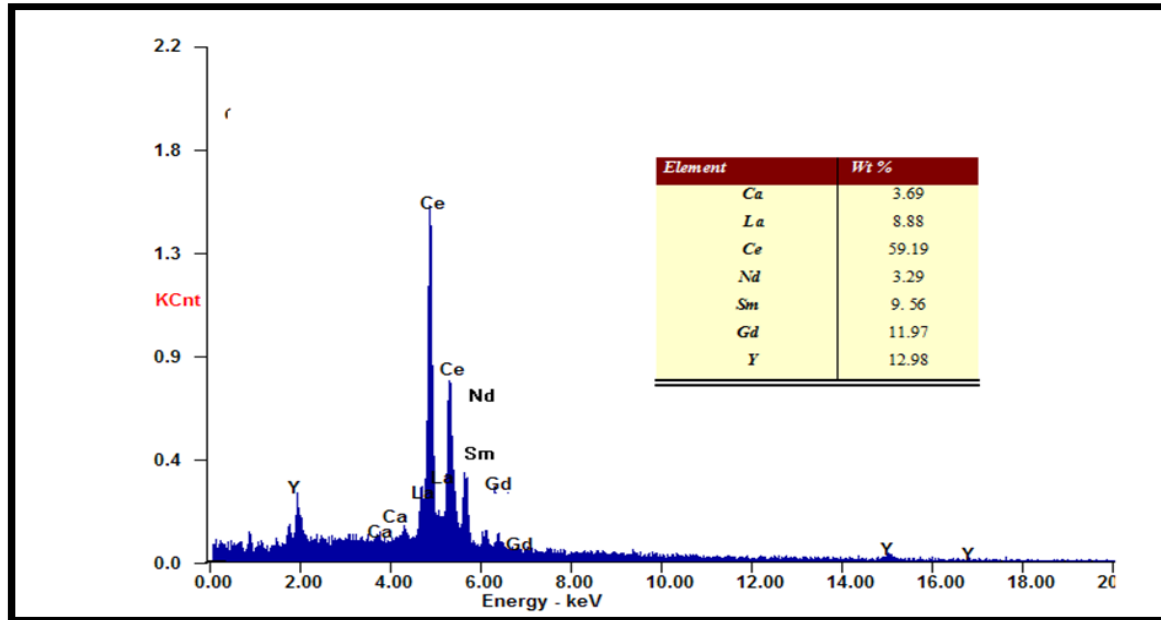


Fig.(3): ESEM- EDX analysis of the prepared Lnsoxide .

4.Conclusion

From the foregoing study, the following general conclusions can be summarized:

- 1– A procedure for separating V from the accompanying Lns can be achieved by breaking down the study spent ore residue by using NaOH at the optimum conditions of spent ore residue / NaOH ratio: 1/3, 3 h. fusion time and 200 °C fusion temperature .
- 2- A procedure for separating Lns from the spent ore residue free from V can be achieved by acidic leaching at the optimum conditions of 80 g/L H₂SO₄ concentration, 120 min. Stirring time within S/L ratio of : 1/3 at room Temp.

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ملخص البحث باللغة العربية

استخلاص الفانديوم واللانثينيدات من التربة اللاتراتيه سابقه المعالجه الغنية بالكربونات موقع أبو ثور
– جنوب غرب سيناء- مصر

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١-هيئة المواد النووية

٢-كلية البنات للاداب و العلوم و التربية-جامعة عين شمس

بعد دراسة المعالجة الكيميائية لاستخلاص اليورانيوم و النحاس التى تمت سابقا على خام التربة اللاتراتيه الغنية بالكربونات بموقع أبو ثور، جنوب غرب سيناء، مصر . تمت ايضا دراسة مكمله لاستخلاص المعادن الهامة المتبقية و هى الفاناديوم و العناصر الارضية النادرة و تركيزاتهم هى 1050 جزء فى المليون فاناديوم و 649 جزء فى المليون عناصر ارضية نادرة و ذلك على مرحلتين متتابعتين ، الاولى هى عملية اذابة قلووية لعنصر الفاناديوم باستخدام هيدروكسيد الصوديوم ثم تبعتها عملية استرجاع عن طريق الترسيب على هيئة اوكسيد الفانديوم ، ثم المرحلة الثانية و هى اذابة العناصر الارضيات النادرة باستخدام حمض الكبريتيك و استرجاعها عن طريق الترسيب الحصول على منتج نقى من اوكسالات الارضيات النادره .