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RESEARCH ARTICLE

Thermal and Acid Oxidative Strategy to Recovery Selenium and Silver from Eucairite CuAgSe

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ABSTRACT:
Sulphides and selenides are mineral species that commonly occur together in natural deposits, according to the relative abundance. Moreover, the emerging importance of selenium in several fields of sciences, the economic value of the metal silver, commonly associated to selenide by chemical affinity and the existence of selenium deposits in Argentina lead to study the CuAgSe eucairite oxidation process in air atmosphere, by thermal and acid treatments in order to the Se and Ag recovery. The analysis was carried out with pure mineral by means of (TGA-DTGA) Thermogravimetric technique, X-ray Diffraction (XRD), Infrared Spectroscopy (FTIR), Chemical analysis, Scanning Electron Microscopy (SEM-EDS) and treatments with HCl, H_2SO_4 and HNO_3 (0.1 M, up to 180 min and 60 ºC). Thermal oxidation permits the separation of $SeO_2(g)$ from a solid residue in the 500-750 ºC range, whereas the adequate combination of soft acid and thermal treatments can be formulated as a potential strategy to separate Agº from a copper (II) solution.

KEYWORDS: Eucairite, thermal effects, acid oxidative effects, TGA and FTIR studies.

INTRODUCTION:

Although the oxidation of sulphide minerals with economic importance is well known, the information about the behavior of selenides is scarce, which occur in nature, in lower amounts, closely associated with majority sulphides and other primary source of metals[1-3].

Whereas the geochemistry of sulphides and selenides is determined by the mineralization and hydrothermal activity, their weathering can be associated to several factors as the formation and leaching of mobile species, the O_2 fugacity, time and temperature. In this context, the stability field of selenides is more restricted than that of sulphide minerals and the differences can be associated to their chemical dissimilarities[4, 5]. The disparities can be observed from the Se and S Eh-pH stability diagrams[5]. The strong oxidant behaviour of the $SeO_4^=$ anion respect to the $SO_4^=$ one, can be related to the lower electronegativity of Se ($E^oSeO_4^=/SeO_3^=$ = 1.15 v, $E^oSO_4^=/SO_3^=$ = 0.20 v), fact that can be associated to the quasi absence of $SeO_4^=$ selenate species in nature. Likewise, whereas the SO_2 is a gas at RT, the SeO_2 is a white solid with a vaporization temperature of 315 ºC.

The thermodynamic stability of Se (IV) in nature shows that chalcomenite, formulated as $CuSeO_3.2H_2O$, is one of the few known selenium oxominerals, although the anhydrous phase is not stable[6].

The occurrence of selenide resources in our country was reported in the past centuries[7, 8]. Conversely, selenium is an essential trace element in human and animal health and nutrition and in this context, during the last decades, it is well documented the importance of Se[5]. Selenium is extensively used not only in medicine but also in other fields such as material sciences and in the agronomical area[9-11].

Unlike the thermal decomposition of metallic selenites[6, 12], the course of selenide transformation is not well known, particularly because in nature the element is found in Se-sulphide deposits. In spite of the importance of Se as well as the economic value of metals associated to selenides (commonly Ag by chemical affinity) aimed us to approach a more detailed study of the thermal and chemical behavior of eucairite mineral, from abundant argentinean deposits. The analysis was carried out by means of (TGA-DTGA) thermogravimetric technique, X-ray diffraction (XRD), infrared spectroscopy (FTIR) and (SEM-EDS) scanning electron microscopy.

MATERIALS AND METHODS:

Eucairite samples proceed from Sierra de Umango, Province of La Rioja, Argentina, one of the first localities of the world where selenide minerals have been found[7, 8]. In this mining district, the first description of the species was made by Klockmann, in 1891, who studied the primary hypogenic selenides: (umangite (Cu_3Se_2), klockmannite (CuSe) and naumannite (Ag_2Se)[8]. Eucairite is associated with quartz and other copper mineral species as silicates, oxides and carbonates. However, pure specimens were carefully hand picked under optical microscope for the study. The selected sample was cleaned to remove soluble impurities, dried at 80ºC and stored adequately. Sample was ground below a particle size of ~ 50µm, to be used in the tests.

The morphology was performed in a Philips 505 SEM electron microscopy instrument with an EDS energy dispersive detector EDAX-9100. Bulk chemical analysis of Cu, Se and Ag was done by ICP AES technique (ChemLab, Canada). Both chemical analyses are in good agreement.

Eucairite was mineralogically identified by X-Ray diffraction analysis (Philips PW 1714 diffractometer, Cu Kα radiation and Ni filter). Datum is in agreement with that reported in PDF 25-1180. "In situ" XRD measurements, working in inert and air atmosphere between RT and 400ºC.

The Shimadzu thermoanalyzer TGA- DTGA 50 was employed for thermal analysis (between RT and 1200 ^{o}C) at a heating rate of 10°C.min^{-1}. Measurements were carried out in dry air atmosphere in alumina crucibles, at a flow rate of 50 ml.min^{-1}. Samples were isolated after arresting the heating process and replaced the oxidizing atmosphere with nitrogen at RT. Morphological and mineralogical changes during the course of the process were followed by SEM-EDS and XRD techniques.

The FTIR infrared spectra were recorded on a Bruker Equinox 55 spectrometer, using the KBr pellet technique, in the 4000-400 cm^{-1} range, with an OPUS/IR software. The spectrum between 120 and 40 cm^{-1} was registered in a Bruker IS-113-V spectrometer by using the polyethylene pellet technique.

Eucairite was also chemically treated with excess of HCl, HNO_3 and H_2SO_4 solutions (concentration 0.1 M). Two experimental variables (temperature and time) were used: 30 and 60°C as well as 30 and 180 min. Mineral residues were washed with distilled water and acetone and characterized by the usual techniques.

RESULTS AND DISCUSSION:

The Cu, Ag and Se values by ICP-AES-chemical analysis (22.44%, 46.56% and 30.99%) were in acceptable agreement with CuAgSe theoretical values (25.38% Cu, 43.08% Ag and 31.54% Se), although this result suggests an empirical formula with a slight Ag excess ($Ag_{1.1}Cu_{0.9}Se$).

Fig.1 shows an amplified photograph with the typical mineralogy of natural samples, previous to the selection. The nature of alteration products was analyzed in detail by EDS and FTIR physicochemical assays, revealing calcite (a), malachite (b), eucairite (c), copper silicate (d), copper oxide (e) and quartz. (f), in agreement with geochemical appreciations[8].

The oxidation study with selected material was made by thermal and soft acid treatments, working in both cases in dry air atmosphere.
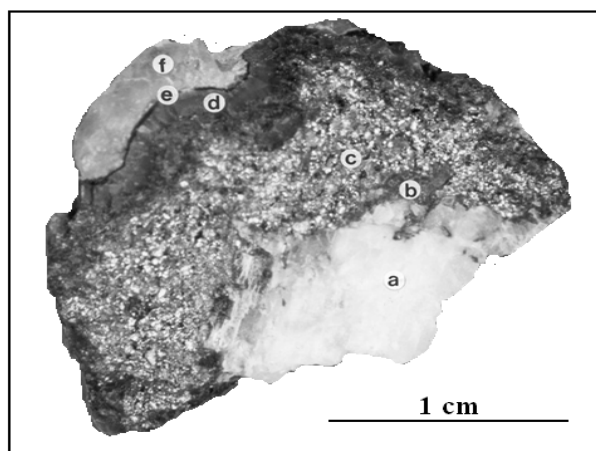
Fig.1: Specimen of eucairite from Sierra de Umango,and its associated minerals: (a) calcite, (b) malachite,(c) eucairite, (d) copper silicate, (e) copper oxide and (f) quartz.

I. Thermal oxidation:

Studies of thermal behavior were carried out under oxidizing conditions, analogous to typical roasting operations, observing that the mineral undergoes a set of sequential reactions as it is observed in a typical TGA-DTGA showed in Fig.2. A series of mass-losses is observed between ~270 and 700 ^{o}C. The first one, between 270 and 400 ^{o}C is weak (~ 1.0 %), but it is followed by two intense and consecutive signals, very difficult to resolve, between 400 and ~700 ^{o}C. The total mass-loss at 1200ºC is 25.72 %. Curiously, no mass gain was observed in the range of studied temperature. The TGA base-line remains constant from 700 up to ~980 ^{o}C, where a slight disruption is observed, surely associated to the Cu (II)-Cu(I) reduction with O_2 evolution. This process occurs at a temperature in the range of Ag melting point (961.9 ºC). It is known that both, Cu(II) and Cu(I) oxides, coexist in different proportion from ~600 ºC, due to the instability of tenorite with temperature increase[13].

Moreover, structural changes are expected in the low region (150-400ºC)[14, 15]. In fact, as another Cu-Ag sulfosalts, eucairite presents a reversible transition close to 200ºC which involves the cell elongation and a consequent atomic re-arrangement where the metal atoms are located in distorted polyhedra. So, it can be suggested that the new framework distribution increases the accessibility of gaseous reagents to the active sites.
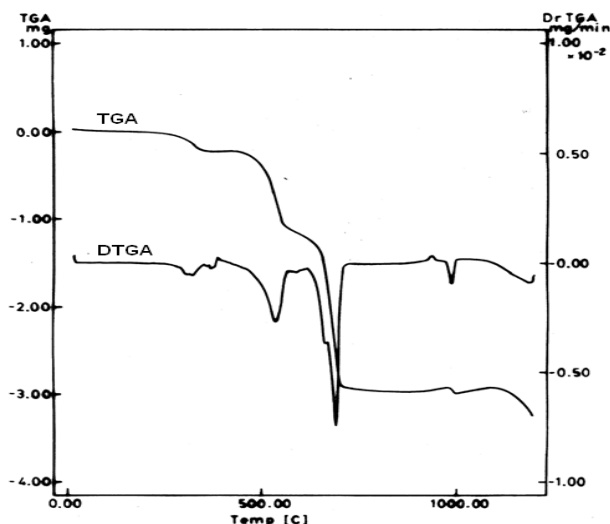
Fig 2: TGA-DTGA pattern of eucairite

TGA-DTGA registered in an inert atmosphere (N_2 stream), between 20 and 300 ^{o}C, showed a slight and continuous mass-loss (0.1-0.3 %), lower than that observed in oxidant atmosphere, but no mineralogical changes were noted by "in situ" XRD analysis.

The behaviour at 400ºC in air atmosphere seems to be related with the copper oxidation and the segregation as Cu(II) phase, in agreement with the paragenetic sequence: AgCuSe (eucairite)-Ag_2Se (naumannite)-(CuSe) klockmannite, proposed by Paar in mineral deposits of La Rioja, Argentina[7]. However, the presence of klockmannite CuSe (PDF 86-1240) was not observed by XRD in the dynamic thermal process. In fact, the Cu(I) $\Rightarrow$ Cu(II) oxidation can be also associated to the simultaneous $Se^=$ oxidation to give Se(IV), with the formation of an instable and amorphous Cu(II)-Se(IV)-O phase. In this sense, it is interesting to remark the reported thermal instability of chalcomenite $CuSeO_3.2H_2O$, with the water loss in two stages: 2/3 mol of water in a first step, while the second dehydration is accompanied by the decomposition giving $2CuO.SeO_2$, a non stoichiometric product containing up to 80 % excess of CuO[6]. In our case, only the progressive decrease of the XRD pattern resolution is observed by heating up to 450ºC.

It is evident that the geochemical affinity favors the surface formation of Cu(II)-$O^=$ and Ag(I)-$Se^=$ clusters, which, by a further heating in an oxidizing media (up to 500ºC), become copper (II) oxide and Ag_2SeO_3 (PDF 82-2226). However, it is also known that the stability of this last phase decreases as temperature increases, leading Agº and SeO_2(g) in the 690-960 ºC range, in agreement with literature data[6, 12].

Oxidation and reduction properties seem to drive the thermal behavior of eucairite (E^o [Ag_2SeO_3/Ag] = 0.36 v and E^o [Cu(II)/Cu(I)] = 0.158 v), increasing the stability field of tenorite (CuO).

From the quantitative point of view, at 531 ºC the mass-loss reached 8.6 %, value that agrees with the selenium release, equivalent to 0.2 mol of SeO_2. This seems to be the reason why Cu-Se-O phases, were not revealed in the 450-500 ºC region. It is very difficult to isolate a crystalline phase in a dynamic process where the SeO_2 evolution is simultaneous with copper oxidation and silver selenite formation.

The FTIR spectroscopy was a good technique to differentiate steps of eucairite oxidation. FTIR active phases between 4000-400 cm^{-1} do not exist for pure natural eucairite. Similar behavior was observed for the samples heated in air up to 300-400 ºC. It is interesting to denote that FTIR spectra of samples original and heated at ~400 ºC, registered between 120 and 40 cm^{-1}, shown in Fig.3, present a slight shifting of the bands, which can be attributed to structural changes during the atomic re-arrangement in eucairite transformation.

FTIR technique suggests the incipient formation of a Se oxo-compound from the weak and broad band centered at ~700 cm^{-1}, observed in samples heated at ~450 ºC.
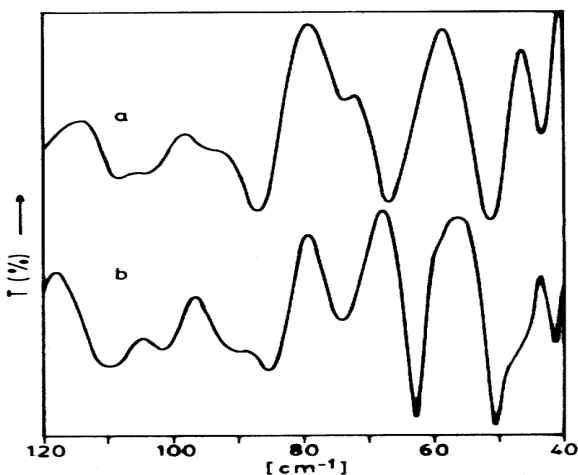

Fig.3: FTIR spectra (between 120-40 cm^{-1}):a) natural eucairite, b) eucairite heated at 400 ºC

Fig.4 shows the comparative FTIR spectra of samples heated at 500 ºC, 1h and 600 ºC 72 h. At 500 ºC, incipient FTIR signals between 400-800 cm^{-1} were observed. However, the sample heated at 600ºC shows a well defined spectrum, characterized by the presence of bands in the 700 cm^{-1} region, attributed to the selenite anion,[6, 12, 16]. Weak bands in the 500 cm^{-1} region can be attributed to copper in oxide environments (Cu_2O at 617 cm^{-1} and CuO between 570-450 cm^{-1} [17]. The ν_2 and ν_4 bending vibrations of the selenite group were observed between 432-320 cm^{-1}. A series of weak bands above 800 cm^{-1} could be associated to Se-O overtones and combinations.
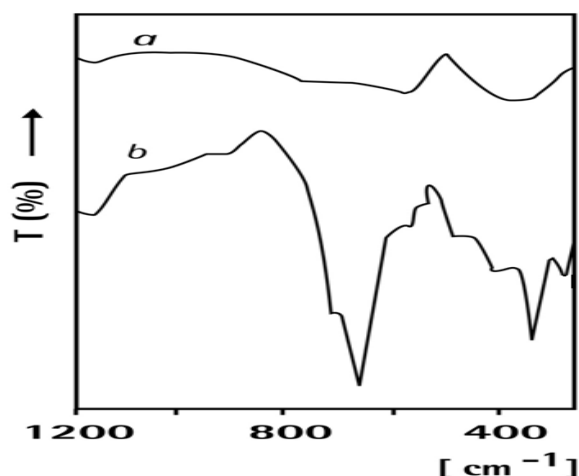
Fig. 4: FTIR spectra (between 1200- 250 cm^{-1}) of eucairite treated at: a) 500 ºC 1 h b) 600 ºC 72 h

Fig.5 shows comparatively the morphological changes during the thermal process observed by SEM technique. A detail at higher magnification of the material treated at 1100ºC is shown in the left upper corner of Fig 5.d. The formation of new species on the surface is followed by softening and melting processes. The higher temperature clearly reveals the presence of liquid metal phase (Ag).

EDS data of Cu, Se and Ag in original and heated eucairite samples are given in Fig.6. Selenium gradually diminishes up to ~ 850 ºC.

The Cu and Ag variability in the 550-650 ºC range was attributed to the atomic heterogeneity and complexity at surface level with the co-existence of two or more phases, randomly distributed over an eucairite core. In fact, the average Ag value was 15 % but values are ranged between 7.20 and 58.70 %. On the other hand, the average Cu value was 72 %, with correlative data for the extreme Ag values of 90.50 % and 19.74 % respectively. Extreme values are not common but are useful to point out variations in the surface composition. It is interesting to note that the highest Cu content was always associated to a lowest Se content (2.30 %) whereas the highest silver content was related to the highest Se content (21.56 %). The Ag/Se ratio (expressed as elemental mass %) close to 2.72 was comparable to that observed in the Ag_2SeO_3 phase (theoretical value = 2.80).

The Se diminution from ~250ºC occurred with a simultaneous increase of Cu content in agreement with the oxidation of copper (I), segregated as CuO. This phase seems to be dispersed on the Ag_2SeO_3 surface. However, from 600ºC the Ag increase is associated to the Ag_2SeO_3 decomposition and Ag reduction. Thus, as the temperature increases (>900ºC), the progressive aggregation of Ag drops, anchored on copper oxides, changes again the trend for the metal EDS chemical values. This can be attributed to the different specific gravity of phases (10.5 g.cm^{-3} for metal Ag and lower values for copper oxides). In fact, XRD pattern at 1100ºC reveals the presence of Ag and tenorite as majority copper oxide.

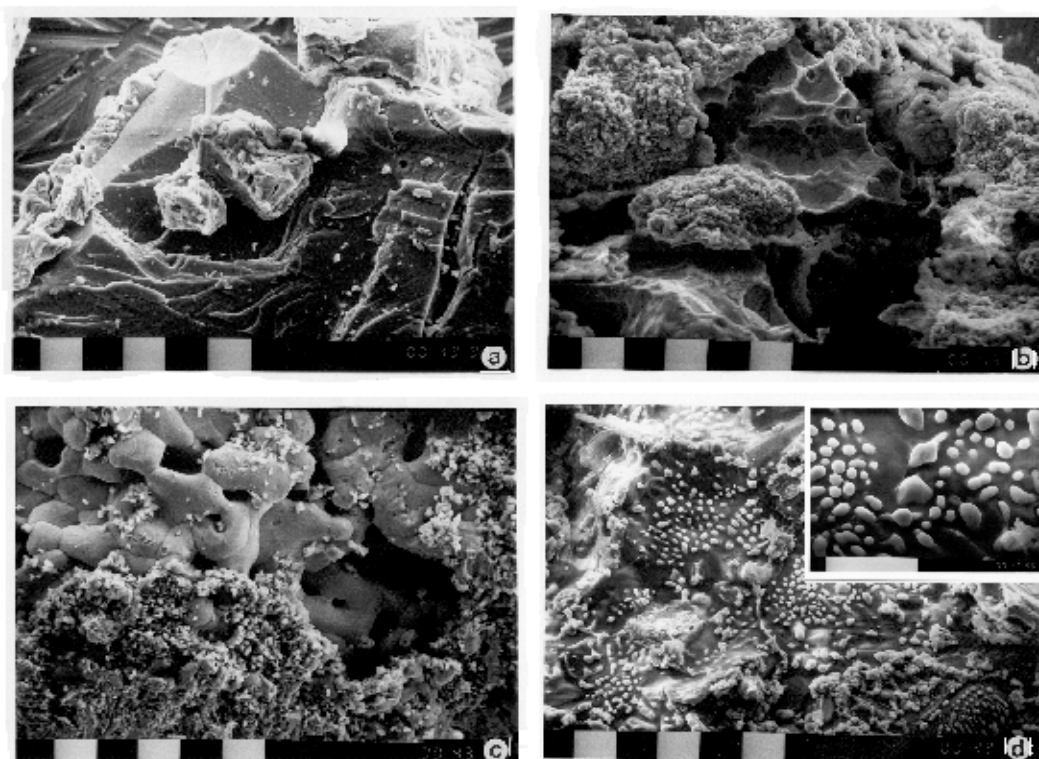**Fig.5: SEM micrographs of eucairite (x 1000, 10μm):**
a)original , b) thermally treated at 600 ºC, c) 900 ºC and,d) 1100 ºC with a detail (x 5000 - 10μm) in its left upper corner.
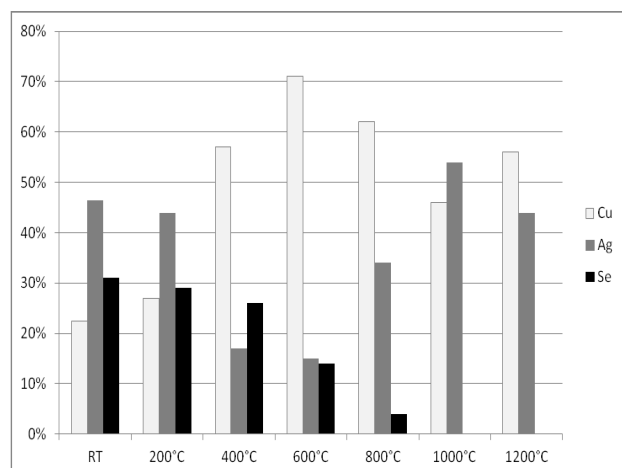
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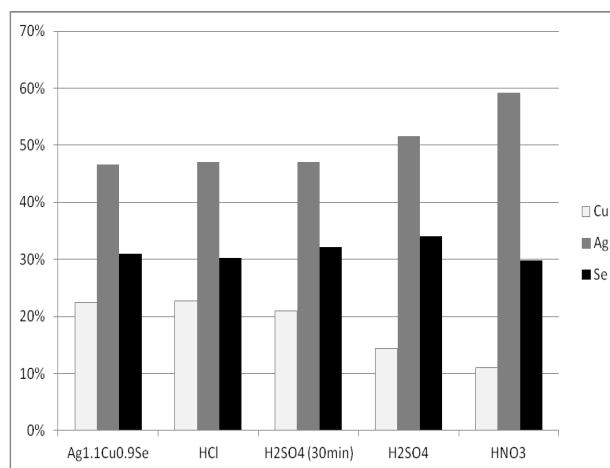**Fig. 6: EDS results (% of element) vs. treatment temperature (in °C)**

Fig. 7: Comparative EDS of the natural sample treated in different acids 180 min (Results for treatment with H$_2$SO$_4$ during 30 minutes are included)

II Oxidative leaching with acid solutions:

It is expected that the treatment with acid leads to chemical reactions depending on the acid strength and experimental conditions[18]. In order to evaluate the magnitude of these processes, several comparative tests were briefly analyzed.

II.a.-Treatment with HCl:

Eucairite dissolved very slowly in the HCl 0.1M at 60 °C during 180 min. The XRD pattern of the residue was similar to that of eucairite, with EDS data observed in Fig.7.

II.b.- Treatment with H$_2$SO$_4$

From treatment with SO$_4$H$_2$, no definite structural alteration of eucairite was observed in the range RT-30 °C (30 minutes). However, the dissolution was effective by longer heating or higher temperatures. EDS results of the mineral residue after heating at 60 °C (30 and 180 min) are comparatively given in Fig.7. Chemical data were consistent with an effective copper leaching. The XRD analysis of the residue (30 min) showed a pattern structurally related to eucairite but enriched in Ag. Moreover, for the shorter treatment, the presence of Se-O clusters was discarded by FTIR spectroscopy, (absence of typical bands of selenite species in the 700 cm^{-1} region). However, by further heating or higher temperature, weak bands of selenite species were detected. The effective presence of alteration products was clearly revealed by XRD pattern of the mineral residue heated at 300 °C (2 h), favoring the crystal development. Hence, the majority phases in the experimental conditions were Ag-rich eucairite (at shorter times) and Ag$_2$SeO$_3$ (at longer times).

II.c.- Treatment with HNO$_3$

Comparative EDS data, shown in Fig. 7, reveal that the oxidizing effect of nitric acid led to the highest copper leaching and a fast formation of Ag-Se-O phases (observed from 30 min treatment). XRD analysis was dominated by the presence of silver selenite (by a heating treatment of the residue, as in the case of H$_2$SO$_4$ leaching), whereas very weak XRD lines of eucairite phase were detected.

DISCUSSION AND CONCLUSIONS:

The reaction sequences, according to experimental conditions, can be formulated as follows:

Thermal process:
Heating in dry air atmosphere, the process occurs in the following steps:
195 °C: Cu$_{0.9}$Ag$_{1.1}$Se (I)   →   Cu$_{0.9}$Ag$_{1.1}$Se (II)   phase transformation
270 – 400 °C: no appreciable reaction
400 – 600 °C: Simultaneous processes can be formulated:
i) Cu(I)-Cu(II) oxidation.
ii) Surface reaction CuSe →Cu-Se-O (amorphous).
iii) Cu-Se-O phase → CuO with evolution of SeO$_2$
iv) Ag-rich selenide → Ag$_2$SeO$_3$
600-750 °C: decomposition of Ag$_2$SeO$_3$ → Ag° + SeO$_2$ + ½ O$_2$
~1000 °C: Partial reduction of Cu(II) (CuO >Cu$_2$O), Ag$_{(s)}$ fusion

The experimental mass loss to give Ag° and copper oxides as final products is 25.72 % in agreement with the theoretical value (25.33%).

In the range between 400-600 °C the dynamical thermal process does not permit the reliable characterization of some products. However, the formation of Ag$_2$SeO$_3$ and CuO can be revealed by XRD. At 750 °C, silver selenite was decomposed in Ag°, SeO$_2$ and O$_2$ whereas the silver melts by further heating (~ 960°C).

The presence of Ag (I) seems to drive the thermal behavior of eucairite, increasing the stability field of tenorite respect to that of cuprite, so that Cu(II) oxide is yet observed as major phase at the higher temperature reached.

Acid solution treatments:
From the treatments in acid solution it can be remarked that:

Diluted acids affect the eucairite stability in different magnitude, depending on the acid strength, time and temperature of reaction:

i)   HCl does not affect the crystal structure in the more drastic experimental conditions (60ºC, 180 min.)

ii) The effect of H_2SO_4 depends on the time: at 30 min and 60ºC the formation of an Ag-rich eucairite phase is observed, corroborating the AgCuSe (eucairite)-Ag_2Se (naumannite) Paar´s sequence in nature. The Ag_2SeO_3 is observed in the oxidant atmosphere as reaction time increases.

iii) Treatments with HNO_3 lead to the higher leaching of oxidized copper. So, the formation of insoluble silver selenite (kps $_{Ag2SeO3}$ = 1.72 $10^{-16})^6$ determines the course of the process.

Results suggest that the dissolution can be well represented by a shrinking core model, controlled by surface reaction and by the acid strength.

Concluding, thermal oxidation permits the separation of $SeO_2(g)$ from a solid residue (copper oxides and metal Ag), whereas the adequate combination of soft treatments (acid and thermal), shown in Fig.8 can be formulated as a potential strategy to obtain $SeO_{2(s)}$ and Ag $^\circ$, ensuring the removal of soluble cooper (II) through formation of insoluble Ag_2SeO_3 whose decomposition leads to the recovery of the desired species.
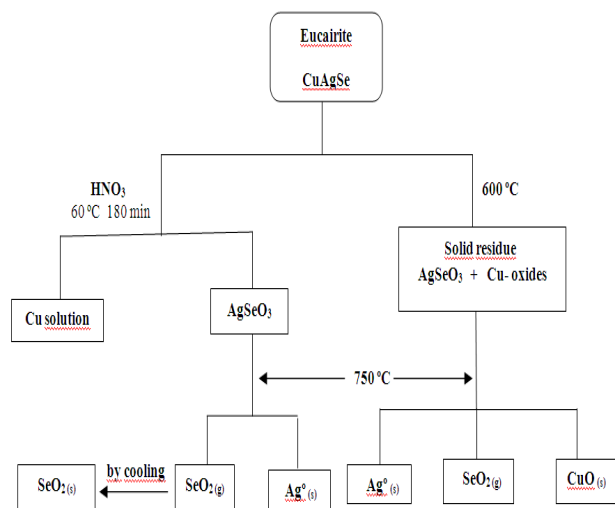

Fig.8: Flow sheet of eucairite acid and thermal treatments

REFERENCES:
1.   Dunn J.G., The oxidation of sulphide minerals, **Thermochim. Acta**. 300; 1997: 127-139
2.   Javeed A., Mohammad A., Mark V., Burton A., Raftery N. A., Hillier J., O'Brien I.H. Understanding, Decomposition Pathways of Mixed Sulfur/Selenium Lead Phosphinato Complexes Explaining the Formation of Lead Selenide, **Journal of Physical Chemistry C**. 115(34); 2011: 16904-16909.
3.   Corkhill C.L., Vaughan D.J., Arsenopyrite oxidation – A review, **Applied Geochemistry**. 24; 2009: 2342-2361
4.   Simon G., Essene E. J. Phase relations among selenides, sulfides, tellurides and oxides;
I,   Thermodynamic properties and calculated equilibria, **Economic Geology**. 91; 1996: 1187-1208
5.   Floor G.H., Román-Ross G. Selenium in volcanic environments – A review, **Applied Geochemistry**. 27; 2012: 517-531
6.   Verma, V.P., A review of synthetic, thermoanalytical, IR, Raman and X-ray studies on metal selenites, **Termochim.Acta**. 327; 1999: 63-102
7.   Angelelli V., Brodtkorb M.K., Gordillo C.E., Gay H.D. Las especies minerales de la República Argentina, Special publication, Servicio Minero Nacional (Argentina). 1983.
8.   Paar W.H., Sureda R., Brodtkorb M.K. **Revista de la Asoc. Geológica Argentina**. 51; 1966: 304-312
9.   Chen L., Yang F., Xu J., Hu Y., Hu Q., Zhang Y. and Pan G. Determination of Selenium Concentration of Rice in China and Effect of Fertilization of Selenite and Selenate on Selenium Content of Rice, **J. Agric. Food Chem**. 50, (18); 2002: 5128-5130
10. Kaim W., Schwederski B. Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life, John Wiley Sons. 1994.
11. Ramoutar R.R., Brumaghim J.L. Antioxidant and anticancer properties and mechanism of inorganic selenium, oxo-sulfur and oxo-selenium compounds, **Cell Biochem Biophys**. 58; 2010: 1-23
12. Okkonen P., Hiltunen L., Koskenlinna M., Niinisto L., Crystal structure and thermal stability of silver selenite, **Acta Chem. Scandinavica**. 48; 1994: 857-860
13. Cotton F.A. and Wilkinson G., Advanced Inorganic Chemistry, Wiley & Sons. 1997.
14. Frueh A.J. (jr), Czamanske G.K., Knight Ch., The Crystalopraphy of Eucairite, CuAgSe, **Z. Krist**. 108; 1957: 389-396
15. Kostov I., Minceva-Stefanova J., Sulphide Minerals, Crystal Chemistry, Paragenesis and Systematics, Bulgarian Acad. Sci.-Institute of Geology, Stuttgart. 1982.
16. Ross S.D. Inorganic Infrared and Raman Spectra, Mc Graw Hill. 1972.
17. Dunn J.G.; Ginting A.R.; Oconnor B.; A Thermoanalytical Study of the Oxidation of Chalcocite, **Journal of thermal analysis.** 41, (2-3); 1994: 671-686
18. Yunmei Y., Yongxuan Z., Williams-Jones A.E., Zhenmin G., Dexian L., A kinetic study of the oxidation of arsenopyrite in acidic solutions: implications for the environment, **Applied Geochemistry**. 19; 2004: 435-444.