IMPROVEMENTS IN PLASMA RAW MATERIAL RECOVERY BY APPLICATION OF THE SELECTIVE IONIZATION CONCEPT

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ABSTRACT

Plasma Raw Material Recovery refers to the possibility of obtain raw materials as pure elements starting from multiple not refined sources such as wastes, minerals and other sort of low grade materials. The concept has been proposed, for very specific applications and always not in its present and general form, in very different fields ranging from nuclear physics to space science. The process implies the ionization of the source materials and the separation of its constituents by electromagnetic means. Some simplifications in the process are possible in manipulating oxides. In this case it is possible to take advantage of the ionization gap between the oxygen and the other constituent metal to reduce the process required power as in the "selective ionization" process theorized by NASA in the '80s. In this paper the energetic feasibility of a direct separation of oxides using Plasma Raw Material Recovery implementing the Selective Ionization concept, hereafter called Enhanced Selective Ionization Method, is evaluated. The general characteristics of the process are described including its physical explanation. The energy required for the oxide dissociation and the separation is calculated separately for each of the main oxides present in the earth crust and hence an assessment of the energy required to separate into pure elements a combination of different oxides is performed along with the indication of the conversion yields.

NTRODUCTION

The possibility to effectively split a material into its elementary constituents, meaning to separate the different atomic elements, has been widely proposed in the past since the '40s. The main purpose was to separate different isotopes of the same atomic species for nuclear purposes, and for this reason many techniques have been developed, ranging from diffusion methods to electromagnetic methods. These latter systems have been developed in the decades to use a wide range of different working models, such as ion beam separation by magnetic field interaction or devices which uses quasi equilibrium plasma on which EM fields are directly applied [1]. Few of these devices have been applied or studied to separate different atomic species rather than only isotopes of the same element. The purpose of this paper is to provide an overview of the devices able to separate useful quantities of material into its constituent components by electromagnetic means, followed by the application of these methods to the recovery of elementary metals starting from oxides, using the possibilities offered by the physics of the phenomena which introduce simplification in the manipulation of the input material. Finally a calculation of the energy requirement to separate a sample of Earth's crust is provided.

Mass separation by electromagnetic means

Technologies to separate atoms of different atomic weight using an interaction of electric and magnetic fields have been developed since WW2 in order to produce material required to be used in the firsts nuclear bombs. Some of these methods are intrinsically not adequate for high mass flow rates or are so extremely expensive in terms of energy requirements that their use outside nuclear programs is impracticable. Other methods have been developed outside the nuclear community for different purposes but they focused interesting aspects of the separation of oxides that can easily applied to other methods in order to increase the raw material recovery yield.

Calutron Massively used during WW2 to produce the ^{235}U for the Hiroshima bomb, developed by Ernest O. Lawrence [2] which got the Nobel prize for the invention of the cyclotron accelerator, this devices uses the same working model of a mass spectrometer, meaning the different cyclotron radius of particles with different charge-to-mass ratio in passing through a constant **B** field. To perform the separation the input material has to be preliminarily ionized and then accelerated to achieve a useful velocity. A first equation used by Lawrence is the simple energy balance between the potential energy provided by an accelerating electric field and the kinetic energy owned by the ions after the acceleration:

$$\frac{1}{2}mv^2 = q\Delta V \tag{1}$$

At this point the cyclotron radius or Larmor radius is introduced, in the second equation:

$$r_c = \frac{mv}{qB} \tag{2}$$

In both equations v has to be considered as the velocity perpendicular to the magnetic field B. As can be seen the higher is the ion mass m the higher is the radius, if single ionization is assumed for all the particles, with constant v and B.

Calutron technology is able to produce a high enrichment yield (requiring a lower number of devices in cascade for isotope separation) but is considered to be energetically expensive.

Problems in this technology are the stream instability due to the space charge limitation: the beam is composed by only positive particles hence to avoid beam instability and divergence due to ions repulsion a background gas is necessary to be ionized by the ion beam an to provide electrons that would keep the beam focused. This problem creates limitation in the throughput [1]. Despite this drawback, if used with different elements rather than isotopes of the same atomic species, the separation is strongly more effective due to the higher radius difference that can be achieved with the same magnetic field: the more the collectors are separated, the highest is the purity of the collected elements. For this reason this technology has been preliminarily considered for the development of a demonstrator able to separate a definite number of elements from incinerator ash [3] by modifying the original concept, substituting the vaporization and ionization stage by electron beam with a plasma torch and an RF plasma ionization stage. The possibility to use a plasma source provides an additional advantage: operating with a quasi-neutral plasma flow solves the intrinsic volume charge limitation, avoiding the necessity of a background gas and increasing the efficiency [4], thank also to a number of configuration with crossed *E* and *B* field different from the Lawrence approach [4][5][6].

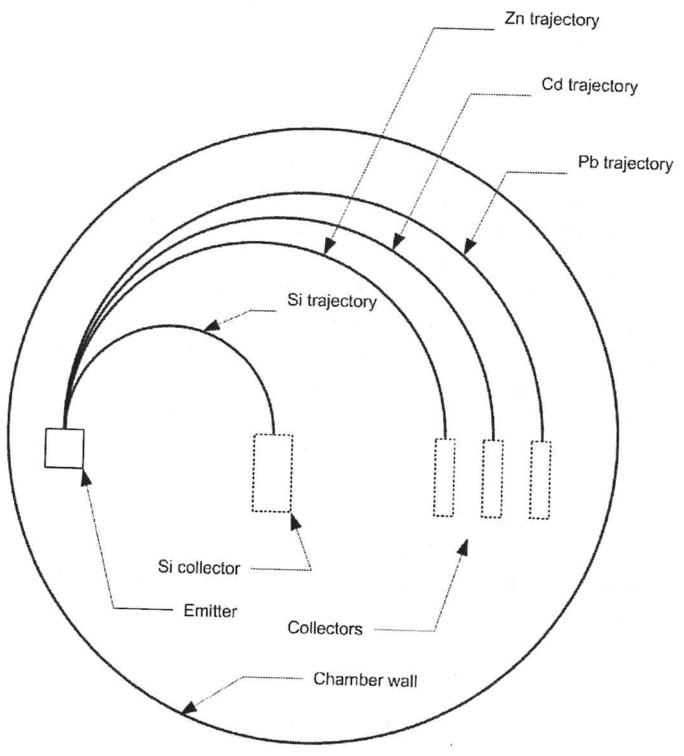

Figure 1. The "Calutron" approach in incinerator ash separation [3].

Selective Ionization Developed by NASA in the '80s [7][8], is mainly addressed to space exploration and to oxygen recovery from In Situ materials found on extraterrestrial planetary bodies. The concept is very close to the initial part of the Calutron system. The material (such are lunar regolith) is heated till vaporization and thermal ionization. At this point to understand the physics of the problem we can refer to Fig.6 in which the ionization potential of the most abundant elements of the Earth's crust is plotted over temperature. It can be seen that at about 10000 K between 40 to 70% of the metals are ionized, while oxygen is below 2%. The Selective Ionization idea is therefore to pass this plasma through an electrostatic field in order to capture at the cathode the positively charged metal ions, while to let the neutral oxygen to continue flowing downstream into a collection system. As can be understood the objective of the Selective Ionization is complementary to the recovery of raw material from a non refined source. In the first case the goal is the oxygen recovery and the metals are seen as a secondary output, while in the second case the goal is the separation of the oxides into the composing atomic species and the oxygen represents the secondary output which can create problems because cannot be easily collected due to its gaseous state at temperatures above 90 K.

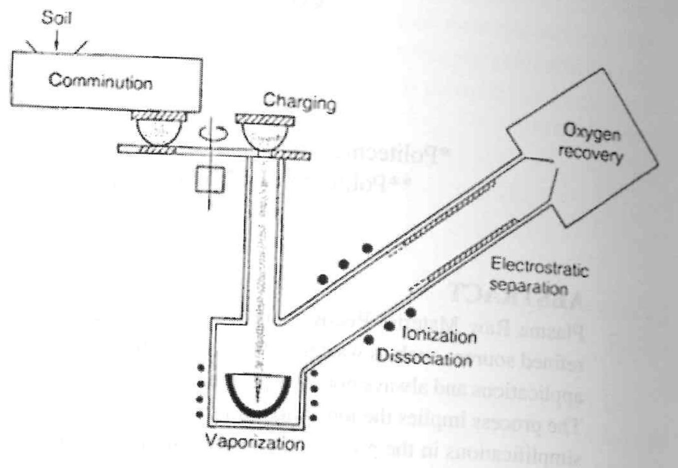

Figure 2. Selective Ionization concept. Courtesy of [8].

Archimedes plasma mass separation The designers of the Archimedes (a proprietary name) concept refer to it as a *plasma mass separator* which purpose is to separate atomic plant waste oxide mixtures ion by ion into two groups: light (not radioactive) and heavy (radioactive) particles. It actually act as a mass filter, because is not able to separate all the elements one by one or to isolate a single ion but it divides all the ions above a certain cut-off atomic weight from the ions below that value, as can be seen in Fig.3.

The process comprises three main passage: a) the melting of the input mixture with a plasma torch till reaching 500 °C; b) the injection and vaporization of the molten mixture thanks to another plasma torch at 5000 °C into the center of the cylindrical filter unit vacuum vessel; c) the ionization and manipulation of the vapor by EM fields inside the filter unit. In the last step heavy particles are swept radially at the center of the filter and are collected on the cylindrical wall, while light particles are transported toward the bases of the cylinder and here collected [10]. The basic mechanism used by this device is the Larmor radius: inside the filter a longitudinal magnetic field is present, the particles injected at the center start rotating along the magnetic field lines with a cyclotron radius which is proportional to the ion mass according to Eq. 2. The high atomic weight ions have a large Larmor radius and collides with the cylinder wall where are collected and removed, while the low atomic weight ions travels towards the end of the cylinder where are also collected [11].

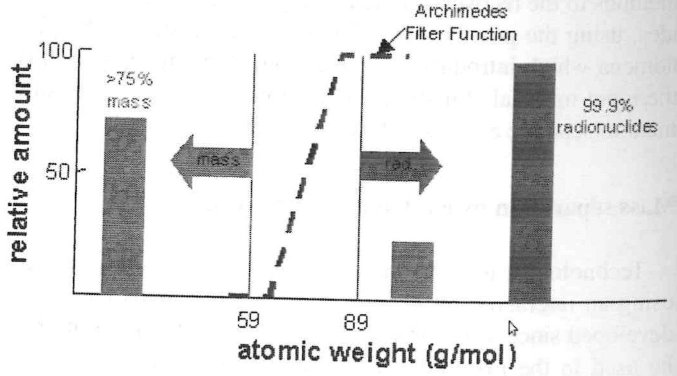

Figure 3. Archimedes Filter function in gap between high atomic weight and low atomic weight (non radioactive) waste. Courtesy of [9].

Plasma Separation Uranium Enrichment The plasma separation process (PSP) has been studied as an isotope separation techniques that makes use of the advancing technologies in superconducting magnets and plasma physics. In this process, the principle of ion cyclotron resonance (ICR) is used to selectively energize the isotope of interest. The source is a plate of solid material which is vaporized by bombarding the plate with energetic ions in a process called sputtering, or a crucible in which the material thermally evaporates and then is ionized by a microwave source. The microwave antenna located in front of the plate energizes free electrons which collide with neutral atoms in the vapor sputtering off the plate, producing a plasma.

The plasma is subjected to a uniform magnetic field along the axis of a cylindrical vacuum chamber as the plasma flows from source to collector. The magnetic field is produced by a superconducting magnet located around the outside of the chamber. The high-strength magnetic field produces helical motions of the ions, with the lighter ions spiraling faster and having a higher ion cyclotron frequency than the heavier ions. As the ions move toward the collector, they pass through an electric field produced by an excitation coil oscillating at the same frequency as the ion cyclotron frequency of the isotope ions of interest. This causes the helical orbit of these ions to increase in radius while having minimal effect on the orbit of the other particles. The plasma flows through a collector of closely spaced, parallel plates. The large-orbit ions are more likely to deposit on the plates, while the remaining plasma accumulates on an end face of the collector (see Fig.4).

The PSP process offers several advantages. A relatively high throughput (several dozens kilograms yearly) is possible due to the quasi-neutrality of the plasma. Moderate to high enrichment is possible in a single pass. Nearly any metallic-like element can be directly processed and recovered on the PSP without the requirement for a gas phase [13].

The only countries known to have had serious PSP experimental programs are the United States and France from the '70s to the '90s for uranium separation, but the programs suffered slowdowns and stops due to the evolution of apparently more readily techniques.

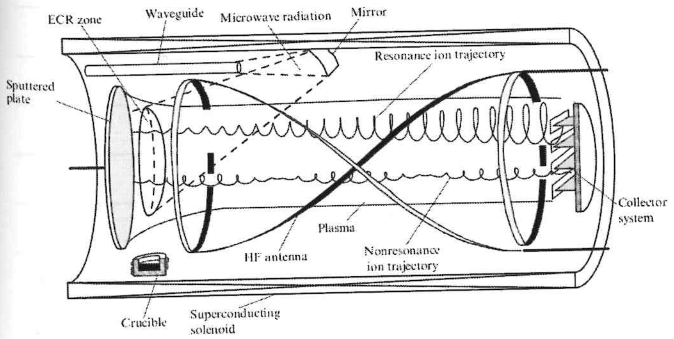

Figure 4. Schematic of the ICR separation process. Courtesy of [12].

INTRODUCING ENHANCED SELECTIVE IONIZATION

The methods explained in the previous section have different goals: to separate isotopes of the same element, to recover oxygen from extraterrestrial planetary bodies, to separate the light and heavy components of nuclear waste for subsequent treatment. In focusing on the recovery of pure elements from oxides, especially metals or metalloids, a combination of the working models of the previous concept can be of great advantage, allowing the obtainment of very high yields. The idea behind Selective Ionization is extremely helpful in removing the most problematic element, oxygen, which has a very high first ionization energy and which is considered an impurity in the recovered metal, even if by itself can be even considered a product if properly collected.

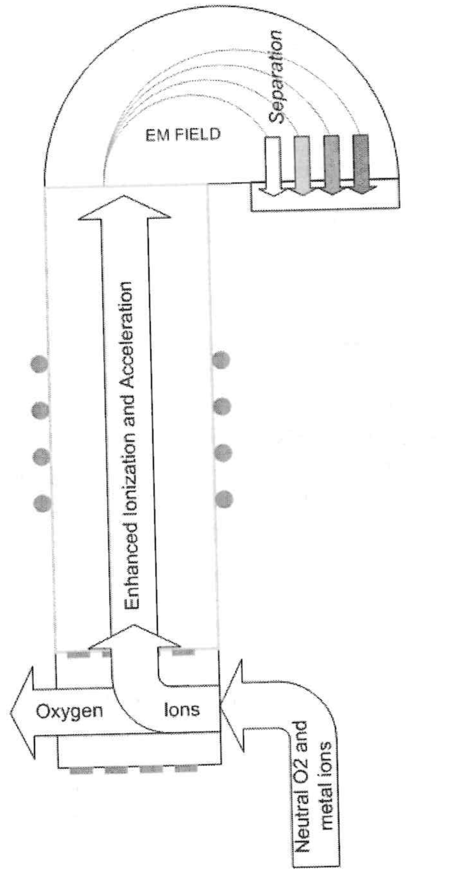

Figure 5. Enhanced Selective Ionization Concept for oxide separation applied to Calutron technology

In a device like the one depicted in Fig.5 devoted to raw material separation, in which the separating material is vaporised and ionized, the metal-oxygen ionization gap can be used to remove the neutral oxygen from the metal anions. The first is insensible to EM fields while the latests are manipulated end extracted according to one or a combination of the methods shown in the previous paragraph. This proposed technique is called *Enhanced Selective Ionization*.

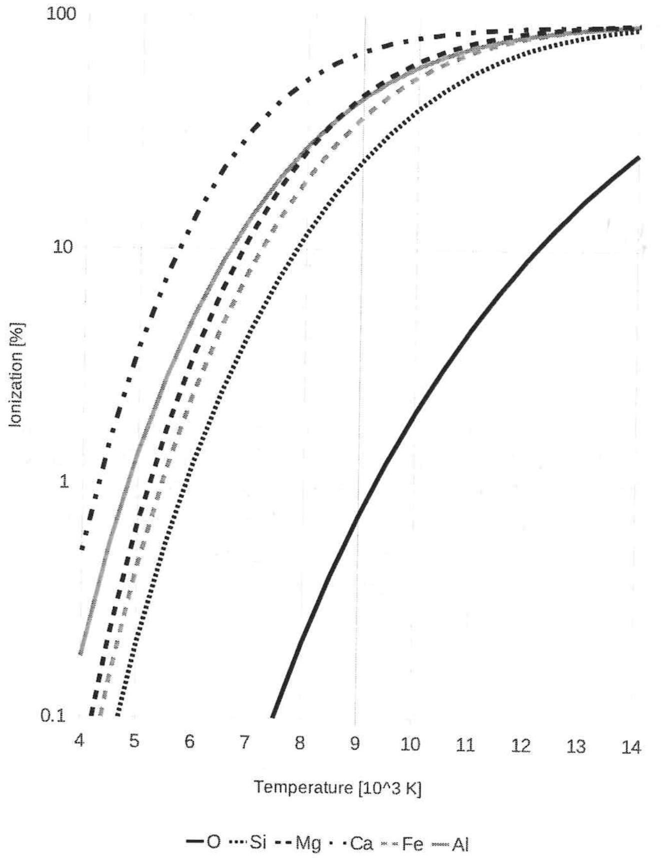

Figure 6. Ionization Vs Temperature of major constituents of Earth's crust at P=1 atm

Figure 6 is obtained considering solely the ionization potential of selected elements, one independent from the other. These curves represent the equilibrium ratio of ionized to neutral atoms vs. temperature, and are obtained using the Saha equation (Eq.3) applied to the single atomic species. Only the first ionization level is assumed in order to have the same mass-to-charge ratio for each atom of the same element for the subsequent separation:

$$\frac{n_i n_e}{n_0} = 2\frac{Z_i}{Z_0}\frac{(2\pi m_e k_b)^{\frac{3}{2}}}{h^3} T^{\frac{3}{2}} \exp\left(\frac{-I}{k_b T}\right) \qquad (3)$$

In Eq.3 the partition functions Z_i and Z_0 are taken from [14]. Fig.6 is calculated in order to reproduce the same image from [8], but despite that a 20% difference in the calculated ionization level at the same temperature and pressure is present, mainly due to the partition functions calculation. Unfortunately in [8] the partition function source is not declared, so no verification can be made.

Fig.6 is the starting point of the Enhanced Selective Ionization Process. At 10000 K the plasma contains a very small percentage of ionized oxygen and an high percentage of ionized metals: the atomic oxygen can be pumped away while the remaining ions can be directed through a separator. Here if for example the input material is only a single oxide, it can be separated from other impurities, such as the oxygen ions, while in case of a mixture of oxides the different elements can be separated one by one.

POWER REQUIREMENT ESTIMATION

To provide an estimation of yields and required power to separate the elements of a sample of typical Earth's crust an approach similar to those used by [8] is considered. The separation process can be subdivide into three phases:

1. vaporization of the input material and atomization at 298 K according to [15]

$$E_{at}(M_aO_b) = -\Delta_f H^0(M_aO_b, 298K) + \\ + a\Delta_f H^0(M(g), 298K) + b\Delta_f H^0(O(g), 298K)$$

2. ionization and temperature rise to equilibrium condition at the temperature T_s required for the separation. It is assumed that ΔH^{T_s-298K} of ions is the same of neutral atoms.

$$E_{\Delta T}(aM(g) + bO(g), T_s) = ai_M E_i^1(M) + bi_O E_i^1(O) + \\ + a\Delta H^{T_s-298K}(M(g)) + b\Delta H^{T_s-298K}(O(g))$$

3. separation of the ions by EM means.

where i_M and i_O are ionization level of the metal and oxygen at the temperature T_s. In place of this calculation we cannot use the lattice energy because it intrinsically includes the enthalpy to convert the oxide to gaseous ions [15], which means for some compounds to go beyond the single ionization required for the separation. As an example for Silica the following reaction occur:

$$SiO_2 \rightarrow Si^{4+}(g) + 2O^{2-}(g)$$

which means to provide from the second to the fourth ionization energy for Silicon and two times the second ionization energy for Oxygen. It is obviously not the case analyzed in this paper.

According to [8] the ionization level at 1 atm and 10000 K are 2.6% for O, 72% for Si, 90% for Al and Mg, 96% for Fe. In this perspective for a sample of minerals which accounts to the 93% of the Earth's crust composition [16], we can calculate the required energy. Tab.1 takes into account point 1 and 2 of the previous calculation procedure.

The total result for a sample of Earth's Crust is of the same order of magnitude of the one calculated by [8] of 11500 kWh/ton, which was actually tailored on lunar regolith.

Table 1. Energy requirement calculation at T_s=10000K. Note: percentages have been renormalized to account for 100% for the energetic calculation.

	E_{at}+$E_{\Delta T}$ kWh/ton	% Earth's Crust	Relative E kWh/ton	
SiO_2	15149	59.97	9773	
Al_2O_3	14456	15.39	2393	
MgO	15214	4.60	753	
CaO	10762	5.41	626	
Fe_2O_3	8778	4.03	381	
FeO	8275	3.56	317	
		Total	**14242**	**kWh/ton**
			0.98	**kWh/mol**
			14.2	**kWh/kg**

Vacuum operation

The previous values are presented as a confirmation of [8] calculation but, being obtained for a pressure of 1 atm, it is very difficult to actually generate a plasma in such condition. With vacuum pumps a pressure on the order of 10^{-3} mbar is appropriate for a relatively dense plasma ($10^{12} - 10^{13}$ cm^{-3}). In this condition the plot of Fig.6 is recalculated and the result is shown in Fig.7. As can be seen despite our conservative partition functions the useful ionization gap is now placed at a temperature of 7000 K, where Oxygen is only 1.4% ionized, Silicon 74% and all the other metals above 90%. In this situation the energy requirement decreases because less energy is used to reach a lower temperature, as can be seen in the results summarized in Tab.2.

Following the approach of [3] to estimate the power requirement of a demonstrator capable of performing such separation we need to take into account an heating system, a pumping device, a ionization equipment and a separation section in which a **B** field is created. Refractory material such as Al_2O_3 requires an heat flux up to 100 MW/m^2 to be vaporized [17]. For a first estimation for a demonstrator an evaporator area of 10 cm^2 can be considered acceptable, requiring about 100 kW of vaporization and ionization power. To heat the plasma we can assume to use as an intermediate stage an antenna as used in the VASIMR Thruster VX-100 experiment [18], in which a 75 kW RF source is used to heat the plasma up to 500 eV thanks to the ion cyclotron resonance mechanism. The required pumping power is can be estimated in 25 kW (Varian NHS-35 pump) while the separation stage was already estimated in [3] in about 25 kW, for a total of 225 kW for about 7.8 kg/h of processed material. The yields referred to single oxides are reported in Tab.3.

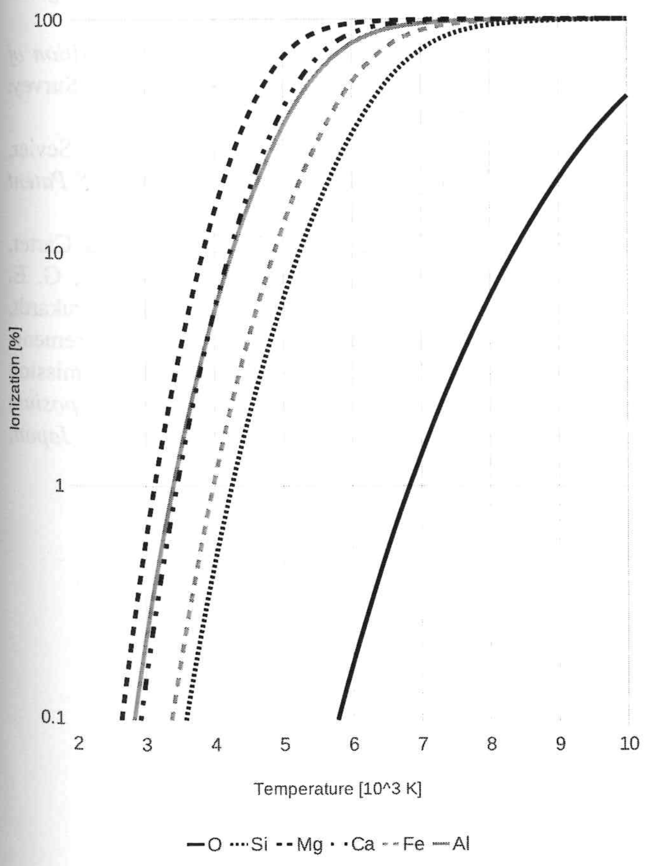

Figure 7. Ionization Vs Temperature of major constituents of Earth's crust at P=10^{-3} mbar

Table 2. Energy requirement calculation at T_s=7000K. Note: percentages have been renormalized to account for 100% for the energetic calculation.

	E_{at}+$E_{\Delta T}$ kWh/ton	% Earth's Crust	Relative E kWh/ton	
SiO_2	13459	59.97	8683	
Al_2O_3	13483	15.39	2232	
MgO	14107	4.60	698	
CaO	9911	5.41	577	
Fe_2O_3	8020	4.03	348	
FeO	7585	3.56	290	
		Total	**12828**	**kWh/ton**
			0.89	**kWh/mol**
			12.8	**kWh/kg**

Table 3. Separation yields for a sample of Earth's Crust soil

	E.Cr. %	Ren %	Mass (kg/h)	M (kg/h)	O_2 (kg/h)	Waste (kg/h)
SiO2	59.97	64.5	5.03	1.73	2.65	0.65
Al2O3	15.39	16.6	1.29	0.66	0.60	0.04
MgO	4.60	4.9	0.39	0.23	0.15	0.00
CaO	5.41	5.8	0.45	0.32	0.13	0.01
Fe2O3	4.03	4.3	0.34	0.21	0.10	0.03
FeO	3.56	3.8	0.30	0.21	0.07	0.03
Total	**92.96**	**100**	**7.80**	**3.36**	**3.69**	**0.75**

CONCLUSIONS

In the presented paper several mass plasma separation approaches are described, introducing the Enhanced Selective Ionization. With this last method an estimation of the required energy to separate a sample of Earth's soil is presented. Production yields appear interesting, with only 0.75 kg/h of wasted material over 7.8 kg/h, which account for less than 10 %. A natural evolution of the concept is the application to a single oxide as an alternative production process of the related metal or metalloid. Higher yields respect to the multiple oxides case are possible due to the tailoring of the separator parameters and the plasma conditions.

NOMENCLATURE

H	Enthalpy (kJ/mol)
ΔV	Accelerating potential (V)
$\Delta_f H^0$	Enthalpy of formation (kJ/mol)
B	Magnetic field (T)
E_i^1	First ionization energy (kJ/mol)
$E_{\Delta T}$	Ionization and heating energy (kJ/mol)
E_{at}	Atomization energy (kJ/mol)
h	Plank constant (J/s)
I	Ionization energy(J)
k_b	Boltzmann constant (J/K)
m	Ion mass (kg)
m_e	Electron mass (kg)
n_0	Neutral density (m^{-3})
n_e	Electron density (m^{-3})
n_i	Ion density (m^{-3})
q	Ion charge (C)
r_c	Cyclotron radius (m)
T	Temperature (K)
v	Ion velocity (m/s)
Z_i	Ion partition function ($-$)
Z_i	Neutral partition function ($-$)

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