POWER DISSIPATION IN HEAVY METALS RECOVERY FROM INCINERATOR ASHES

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ABSTRACT

Under controlled conditions waste-to-energy plants are very useful systems to dispose solid wastes in combination with energy production. For common urban wastes, hence excluding special wastes, the incineration products are fly and heavy ashes where heavy metals are concentrated due to their impossibility to be vaporized. Those metals are usually lost because up to now the common ashes disposal methods have been cement or clay inertization or simple ashes storage in safe places. In order to recover those otherwise lost valuable and useful heavy metals we present the concept of an electromagnetic device able to separate and collect the different atomic species. The proposed device is essentially composed by an atomization stage followed by a separation one. The former atomizes and ionizes ash components allowing the second stage to perform separation of the desired metals by means of an electromagnetic field. Power dissipation represents one of the major issues of such devices due to the high power required to perform species separation. In this paper the major power sources and losses are also identified.

INTRODUCTION

Waste-to-energy plants are widely used in Italy and worldwide to reduce the amount of solid urban wastes. Besides all the consideration about the environmental problems caused by polluted vapors and an economy based on the concept of ”disposal” and not on the concept of ”recycling” or better ”reutilization”, it is a fact that WtE plants’ products are heavy and fly ashes mainly composed by silica and by other compounds containing a variety of elements. These ranges from Calcium and Aluminum to heavy metals like Zinc, Lead and Cadmium. In Table 1 the composition of a typical sample of fly ash is shown. Elements like the aforementioned heavy metals ranges from 0.84% to 0.014%. Such elements represents also a dangerous source of pollution and for this reason fly ashes have been disposed in the past with concrete inertization and comparable means. Hence if it could be possible to remove heavy metals from ashes in addition to recover precious elements, it will be possible to reduce the ashes toxicity, requiring less restrictive, and then less expensive, safety practices.

Compound	**Percentage [%]**	**Compound**	**Percentage [%]**
SiO2	39.1	K2O	2.3
CaO	15	SO	6.9
Al2O3	13.6	Cl	2.4
Na2O	5.5	CO-	0.71
Fe3O4	3.2	Zn	0.84
TiO2	2.8	Pb	0.4
MgO	2.7	Cd	0.014

Table 1: Typical fly ash composition [1]

This paper presents the concept of a device able to separate heavy metals from fly ashes. A preliminary design is performed, along with a first estimation of the required power. Calculations show that the concept, due to the high energy input needed, could be sustainable if, along with heavy metals separation, the recovery of silicon and its purification to high grade level is performed. This process could represent a valid source for electronic grade silicon.

CONCEPT DESIGN

The concept is based on the working model of a mass spectrometer. In the device the material to be processed is raised to a plasma state in order to be manipulated by electromagnetic means. The plasma is then accelerated and subjected to a magnetic field able to separate the different elements thanks to the mass/charge ratio.The proposed device is hence composed by three parts:

1. a source stage where the material containing the metals of interest is heated till vaporization and ionization to a plasma level is attained;
2. an intermediate stage where the plasma is maintained ionized and is accelerated by electromagnetic or electrostatic means;
3. a separation stage where, thanks to a static magnetic field, the heavy metal ions are separated from the unwanted material.

A graphical representation of the concept is shown in Figure 1.

SOURCE STAGE

A consistent approach to the problem of understanding how much atomizing a substance costs comes from the work of Bogatyreva et al. [2] which defines the atomization energy as the work required to break the chemical bonds in the compound

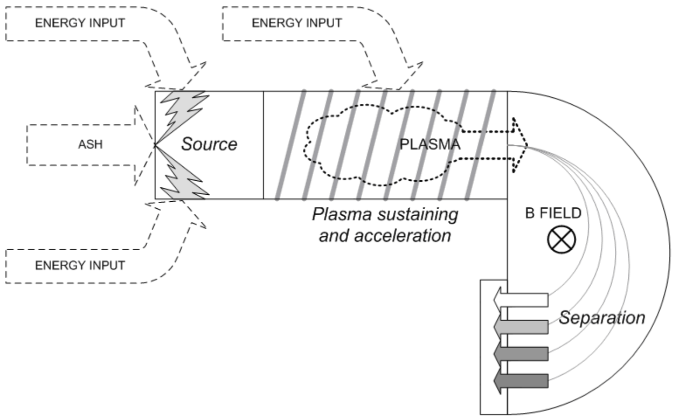

Figure 1: Graphical representation of the demonstrator concept

Element	Mass [kg]	Element	Mass [kg]
Si	1.000	S	0.252
Ca	0.586	Cl	0.131
Al	0.394	C	0.017
Na	0.180	Zn	0.046
Fe	0.127	Pb	0.022
Ti	0.132	Cd	0.001
Mg	0.089	O_2	2.141
K	0.104	**Total**	**5.222**

Table 2: Theoretical elements masses recoverable from 5.2 kg of ashes, corresponding to 1 kg of pure Silicon

with the formation of free constituent atoms. This means calculating the atomization energy by summing up the standard enthalpy of formation of the mineral and the heats of formation of its constituent atoms:

$$E_{at}(M_kX_i) = -\Delta H^0(M_kX_i, 298K) + \\ + k\Delta H^0(M, 298K) + i\Delta H^0(X, 298K)$$

Another interesting concept is represented by the lattice energy. It is usually defined as the enthalpy of formation of the ionic compound from gaseous ions and as such it is invariably exothermic. In case of NaCl, the lattice energy is the energy released by the reaction

$$Na^+(g) + Cl(g)NaCl(s)$$

which would amount to -787 kJ/mol [3]. Some older textbooks define lattice energy as the energy required to convert the ionic compound into gaseous ions which is an endothermic process and, following this definition, the lattice energy of NaCl would be +787 kJ/mol. It is difficult to calculate experimentally the lattice energy due to the impossibility for every compound to prepare gaseous ions, but analytically it can be calculated by several techniques, using the BornHaber cycle or Borns, Kapustinskiis, and Fersmans equations.

In order to correlate the two aforementioned energies we can say that atomization energy differs from lattice energy by the sum of the constituent cation ionization potentials and the electron affinities of all the constituent atoms. It is clear the lattice energy is the value we are looking for in the frame of the separation demonstrator.

Bogatyreva provided an interesting work where the lattice and atomization energies are calculated with different methods. To have a feeling of how these numbers are correct it is possible to find another source of values in the work of Glasser er al.[4] where they use a different method to predict the lattice energy and then this is compared with values calculated with classical methods.

As already described, the average incinerator ashes contain about 40% of silica, 15% of CaO, 13.6% of aluminum oxide and other compounds in lower percentage, including heavy metals. In order to provide a term of comparison, the quantities of each element are referred to the amount of ash necessary to obtain 1 kg of Silicon, the most abundant species except Oxygen. The motivation for this choice, in addition to data representation purposes, is that Silicon, if purified to high grade level for electronic purposes, can represent an important source of revenues that can contribute making affordable such ash disposal technique, in addition to the revenues from metals recovery. Hence to obtain 1 kg of silicon about 5.22 kg of ash is needed. With the percentages shown in Table 1 the amount of other elements recoverable with the same amount of ashes is shown in Table 2.

From the energy count point of view it is possible to fill a

Comp.	Lattice energy* [kJ/mol]	Perc. [%]	Molar mass [kg/mol]	e [MJ/kg]	E (1 kg) [MJ]
SiO2	13467	39.1	0.0601	224.08	87.61
CaO	3536	15	0.0561	63.03	9.45
Al2O3	15597	13.6	0.102	152.91	20.8
Na2O	2519	5.5	0.0398	63.29	3.48
Fe3O4	15027	3.2	0.2314	64.94	2.08
TiO2	13347	2.8	0.2364	56.46	1.58
MgO	3950	2.7	0.0403	98.01	2.65
K2O	2231	2.3	0.0942	23.68	0.54
SO	4000	6.9	0.0481	83.16	5.74
Cl	1256	2.4	0.0355	35.38	0.85
CO-	4000	0.71	0.028	142.86	1.01
Zn	906	0.84	0.0654	13.85	0.12
Pb	716	0.4	0.2072	3.46	0.01
Cd	868	0.014	0.1124	7.72	0
				Total E [MJ]	**135.93**

Table 3: Lattice energy breakdown of the typical incinerator ash composition

* for Zn, Pb and Cd species the sum of the vaporization energy (from std conditions) and the first ionization energy is provided

breakdown of the lattice energy of each compound (Table3), with the related percentage in terms of mass, and calculating in 135.9 MJ the energy cost to ionize ideally 1 kg of ashes. To obtain 1 kg of Si, 0.4 kg of Al, 0.12 kg of Fe, 0.13 kg of Ti, 0.046 kg of Zn and other elements, the total energy cost amounts to 709.8 MJ. This value will be considered in the final energy count.

Source stage power estimation

Practically the source stage will most likely be represented by an electric arc being able to break the ash compounds to their ionic state. This process is often performed in plasma waste treatment with a plasma torch that raises the temperature of a medium gas, usually Argon, up to thousands of Kelvins and it ejects this plasma on the waste to be gasified [5]. Obviously in the present demonstrator it is not possible to utilize an additional gas that would increase the power losses both for ionization, since it needs additional energy to be ionized, and for separation, being shoot into the separator with the other ions. For this reason the solution with only the electric arc is preferable. However, purely for a first estimation purpose, the power of a commercial plasma torch is used.

In order to estimate the amount of energy used in the process, we can assume that mass flow rate is constant in the whole demonstrator. This means that assuming an electric arc of a certain power, and knowing the required energy to ionize 5.22 kg of ash, we can calculate the time needed by the source stage, and then the amount of energy used by all the other stages. Using the specifications of one of the Westinghouse Plasma Corporation plasma torches regarding the required power, we can assume to use a 100 kW device. With such power the time required to process the previously mentioned mass of ash is 1.97 h. This value will be used for all the calculations summarized in Table 5.

INTERMEDIATE STAGE

The intermediate stage is the most difficult to be sized. It is devoted to complete the ash ionization in case neutral atoms remained inside the plasma, and to accelerate these ions for the next separation stage. Theoretically, it can also be avoided if the source stage is able by its own to ionize the highest part of the material and to accelerate the ions to the required speed, thanks to a particular geometry and/or a particular configuration of EM fields. As a preliminary estimation, and as a worst case, we can assume to use as an intermediate stage an antenna as used in the VASIMR Thruster VX-100 experiment [6], in which a 75 kW RF source is used to heat the plasma up to 500 eV thanks to the ion cyclotron resonance mechanism. For the same reason, even if we may need a lower temperature, we are introducing ideally an higher mass flow rate respect to the reference so the same amount of power is maintained as a first estimation for the intermediate stage.

HEAVY METALS SEPARATION

The easiest way to separate materials is to use the cyclotron radius of the different atomic species, shooting the ions in a strong magnetic field in order to bend their trajectories thanks to the Lorentz force. This is very close to the concepts of the firsts mass spectrometers and it is easy to perform some quick calculations regarding the most common atomic species to understand the size of the splitter and the magnetic field intensity.

Following the work of E.O. Lawrence [7], it is possible to size the separator in order to provide the same performance of his device. 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:

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

Lawrence imposed an accelerating potential 4000 times the original thermal energy spread, in order to have the accelerated ions almost with the same energy and to avoid velocity scattering that would bring to different ion path. He used a ΔV of 25 KV and assuming ions on average are ionized only one time, in order to approximately have for every ion the same mass-to-charge ratio. At this point the cyclotron radius is introduced, in the second equation:

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

In both equations v has to be considered as the velocity perpendicular to the magnetic field B. In our case, we have an intermediate stage that provides the required inlet velocity, but we assume to be able to set the RF source to provide the save value that comes out from Eq. (1) for each considered species.As already observed, atoms are uniquely considered to be ionized only once.

Using the above two formulas, calculating the inlet speed from the first and inserting this result into the second, it is possible to calculate for every atomic species the cyclotron radius with the assumptions of using a 25000 V electric field and an electric field of 0.3 T. The latter value has been chosen always

					13	14
					Al	**Si**
					27.0	28.1
[- - - -	- VIIIA -	- - - -]	IB	IIB	**0.394**	**0.402**
26	27	28	29	30	31	32
Fe	**Co**	**Ni**	**Cu**	**Zn**	**Ga**	**Ge**
55.8	58.9	58.7	63.5	65.4	69.7	72.6
0.567	**0.583**	**0.581**	**0.605**	**0.614**	**0.634**	**0.647**
44	45	46	47	48	49	50
Ru	**Rh**	**Pd**	**Ag**	**Cd**	**In**	**Sn**
101.1	102.9	106.4	107.9	112.4	114.8	118.7
0.763	**0.770**	**0.783**	**0.788**	**0.805**	**0.813**	**0.827**
76	77	78	79	80	81	82
Os	**Ir**	**Pt**	**Au**	**Hg**	**Tl**	**Pb**
190.2	192.2	195.1	197.0	200.6	204.4	207.2
1.046	**1.052**	**1.060**	**1.065**	**1.075**	**1.085**	**1.092**

Table 4: Larmor radius of some elements for B=0.3 T, ΔV=25000 V

following Lawrence indications but also because, in order to design a technology demonstrator, the goal is to minimize the device dimensions ad the required power. The drawback of this requirement is that the requested magnetic field has to be strong enough to allow the ions to perform a 180 turn with a reasonable length. In fact in this way the ions with the same inlet speed and same mass/charge ratio but slightly different inlet angle at 180 from the starting point collide in the same position, even if they describes slightly different trajectories. For this reason a value of 0.3 T is able to keep the ions cyclotron radii within a diameter of 3 m. In Table 4 a sort of special periodic table is shown, reporting in bold the cyclotron radius in meters of the most interesting elements contained in the ash.

Focusing only on the atomic elements of interest, it is possible to see that their radii differ on the 5-10 cm or more one from each other, meaning that the ending spots are greatly separated one from each other, easing the collecting problem. A couple of solenoids is assumed to be used to create the magnetic field of 0.3 T necessary for the separation. We used the simple formula for the calculation of the magnetic field inside a solenoid

$$|B| = \mu \frac{N}{h} I \text{ hence } I = \frac{Bh}{\mu N}$$

where h is the solenoid length, I the current, N the number of loops. In order to estimate a worst case we assume not to have any core in the solenoid , meaning that $\mu = \mu_0 \mu_r = 4\pi \cdot 10^{-7} \frac{N}{A^2}$.

The electrical resistance of the wire used for the loops is

$$R = \rho \frac{l}{A} = \rho \frac{l}{\pi r_w^2} \text{ with } l = 2\pi r_d N$$

being r_w the wire radius, l the wire length, with a resistivity $\rho = 1.72 \cdot 10^{-8} \Omega m$ such as copper and r_d the overall magnet radius, higher that the Larmor radius of the heaviest atomic species the device is built to separate. In our case it is $r_d = 1.5m$. We obtain the requested power as

$$P = V_w I = I^2 R = \left(\frac{Bh}{\mu R} \right) \frac{\rho l}{\pi r_w^2} = 12.3kW$$

This value has to be multiplied by two for the two solenoids, calculated for $N = 600$, $r_w = 1mm$, $h = 5cm$. The schematic in Figure 2 gives a graphical representation of the characteristic lengths.

PUMPING ENERGY ABSORPTION ESTIMATION

To maintain the required vacuum level a diffusion pump and a backup pump are needed. As a reference the pumps from Varian Inc. are chosen. In order to select the appropriate pump the volume between the magnetic coils was calculated, resulting equal to about 700 dm^3. For this value, we can use a diffusion pump like the Varian HS-2 with a pumping speed range of 160-200 m^3/s. This pump requires a backup pump of minimum 8.5 m^3/h, like the rotary vane pump Varian DS 302. The overall energy cost is 450W for the diffusion pump, and 450 W for the rotary vane pump, with a total required energy for 1.97 h operations of 1.77 kWh.

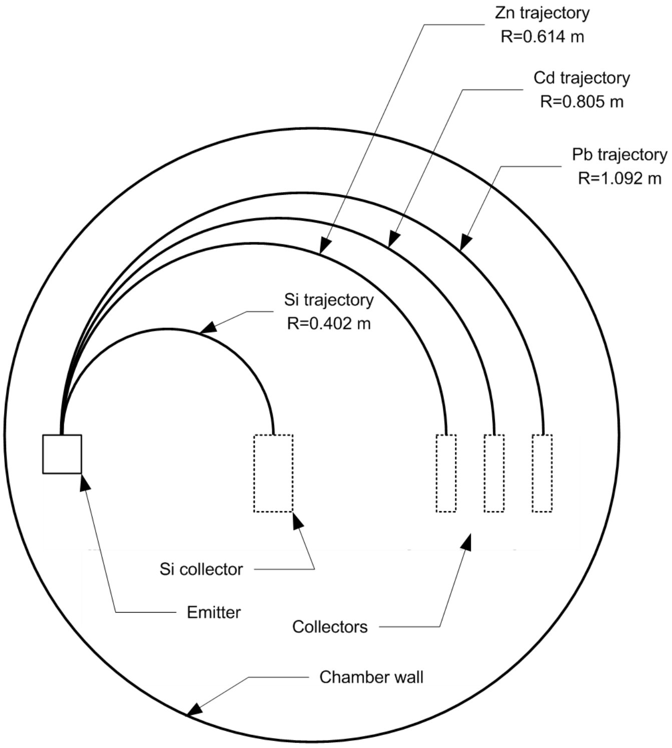

Figure 2: Graphical representation of the chamber with the most important dimensions for B=0.3 T, ΔV=25000 V

PROCESS ENERGY ESTIMATION

Following all the considerations exposed in the previous sections it is possible to fill a breakdown in Table 5 summarizing all the energy costs for processing 5.22 kg of ash in order to recover the elements in the quantities listed in Table 2.

Assuming a worst case of 75% losses between energy and mass losses to obtain high purity grade silicon we can safely consider a total of 5690 MJ the energy required by the process. As a reference in case the only element of interest is not the heavy metals but the silicon, the previous value has to be compared to the energy required to obtain 1 kg of pure Silicon with a conventional process [8] which amounts to 7668 MJ, i.e., 1.34 times higher value. The additional benefit consists in obtaining other valuable pure raw materials.

As it can be seen, the power involved is on the order of 200 kW. Adequate means for removing the dissipated power are necessary for every stage. The former two absorb 175 kW. In case of a single atom species involved in the process, the RF coupling could be set at a very high efficiency level, but in case of multiple species this could not happen. In both cases we shall consider a 30-40% power losses, resulting in a heat flux that has to be removed. From the separator stage point of view the 25 kW involved are completely due to Joule heating, hence also in this case adequate cooling has to be provided in order to avoid the wire to be overheated. Regarding the source stage, if the arc and the plasma can be designed in order to be adequately confined by self induced or external electromagnetic means, the flux is mainly represented by radiative heat flux from the plasma core. This flux would likely heat the source stage walls, which shall be designed to be able to sustain an high temperature and not necessarily this must be considered a drawback. In fact too cool the chamber walls would likely recombine the plasma ions introducing higher inefficiencies into the process, while a

Source stage				
moles of Si in 1 kg	35.71	*mol*		
kg of ash to obtain 1 kg of Si	5.22	*kg*		
energy required	709.81	*MJ*	197.17	*kWh*
power available	100.00	*kW*		
time required	1.97	*h*	7098.08	*s*
Intermediate stage				
power antenna	75.00	*kW*		
energy required intermediate	532.36	*MJ*	147.88	*kWh*
Separation stage				
power separation	24.51	*kW*		
energy required separation	173.95	*MJ*	48.32	*kWh*
Pumping power				
diffusion pump power	0.45	*kW*		
rotary vane pump power	0.45	*kW*		
energy required	6.39	*MJ*	1.77	*kWh*
Total				
Total required energy	1422.51	*MJ*	395.14	*kWh*
Power required	200.41	*kW*		

Table 5: Device required energy estimation

hot chamber wall would help in heating the neutral atoms still present in the region. Hence the cooling system has to be designed in order to keep the walls to the required temperature, and an effort shall be made to choose adequate materials able not to erode and not to interact with the plasma but able to sustain a very high temperature.

CONCLUSIONS

The concept of a device able to separate by electromagnetic means the elements of a typical incinerator ash is presented. The preliminary evaluation about the power needs and sizing was performed. Preliminary calculations seem to show the power requirements are lower than a traditional process for silicon production. The additional advantage is that other valuable resources such as Al, Fe, Ti , Zn, Pb are recovered, lowering the toxicity of the ashes that can be disposed in a safer manner. The drawback is represented by the processing time, higher than traditional means. The most relevant power losses was identified and considerations are made on the involved heat fluxes also from the design point of view.

NOMENCLATURE

A	Wire cross section (m^2)
B	Magnetic field (T)
E_{at}	Atomization energy (kJ/mol)
h	Solenoids length (m)
ΔH^0	Enthalpy of formation (kJ/mol)
I	Current (A)
l	Wire length (m)
m	Ion mass (kg)
M_k	Species constituents the M_kX_i mineral
N	Solenoids number of loops ($-$)
q	Ion charge (C)
R	Wire electrical resistance (Ω)
r_c	Cyclotron radius (m)
r_d	Separator stage/solenoids radius (m)
r_w	Wire radius (m)
v	Ion velocity (m/s)
ΔV	Accelerating potential (V)
X_i	Species constituents the M_kX_i mineral
μ	Magnetic permeability (N/A^2)
μ_0	Vacuum magnetic permeability (N/A^2)
μ_r	Relative magnetic permeability ($-$)
ρ	Electrical resistivity (Ωm)

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