Technical possibilities to support separation of radioactive elements from metallic waste

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Abstract
In the nuclear industry metallic objects can be either surface or bulk contaminated. Surface contaminated objects are often decontaminated by chemical or mechanical means, but are there other possibilities?

During melting slags are formed either spontaneously or by adding slag forming compounds. However, one question that frequently arises is:
Can all nuclides be separated by adding slag forming compounds?
This question is not entirely correct as it is not only the radioactive nuclides that are separated from the metal but all atoms of that element present in the melt, radioactive and stable isotopes alike.

Part of the answer lays in thermodynamics. Thermodynamics cannot positively answer the question with yes, as there are also practical and economical aspects to take into account, but if the answer is no there will never be any practical or economical efforts that will override nature.

This paper will describe the theoretical baseline for evaluating the possibilities to separate certain elements during the melting process, mainly from steel but other metals will also touched on. The most common elements that have radioactive isotopes of interest is of course cobalt (Co-60), but other elements of interest are manganese (Mn-54), strontium (Sr-90), antimony (Sb-125) and of course heavy elements such as uranium, plutonium and americium.

The paper will also describe methods used in the normal metal melting industry to separate elements from the base metal melted. This section will cover practical methods used as well as developed methods that are very seldom used due to time or financial constraints.

Introduction

Metals used in the nuclear industry are usually of a very good quality and the numbers of alloys are limited. As nuclear power plants are being decommissioned these metals should be possible to recycle. Decontamination of metals that are only surface contaminated can be done by several methods for example chemical decontamination, with methods such DfD[1], CORD or CanDecon, it can be done in-situ or in a specific facility or by mechanical means as blasting by grit, high pressure water or glass beads always done in specialist facilities.

However, even after a normal decontamination there will be radioactivity still left on the surface and depending on the surface structure thus might be more or less. As the metals are melted for homogenization some nuclides, or more correctly some metal elements, decontaminates spontaneously and some with the help of slag forming agents. During this decontamination the nuclides are transferred to the slag phase or as vapour to the dust. Other metals will go into solution in the liquid base metal and are not separated will not separate or separates only to a small degree. The thermodynamic properties of the base metal and the nuclide control this behaviour. One important property is the base metals possibility to dissolve other metals. Both carbon as well as stainless steel is great solvent of other metals in comparisons with aluminium, cupper and lead. Hence, the focal point of this paper will be on the behaviour of different nuclides together with steel.

Special emphases will be on the most common elements that have radioactive isotopes in steel. Table 1 shows the nuclide distribution of these elements from remelting of contaminated steel scrap [1].

Table 1
Nuclide distribution from steel scrape [1]

Nuclide	Steel (%)	Slag (%)	Dust (%)	Other (%)
Mn-54	24-100	1-75	0-5	0
Co-60	20-100	0-1	0-80	0
Zn-65	0-20	0-1	80-100	0
Sr-90	0-20	95-100	0-10	0
Ag-108m	75-100	0-1	0-25	1 (bottom)
Sb-125	60-100	0-20	10-40	0
Cs-137	0	0-5	95-100	0
U	0-1	95-100	0-5	0
Pu	0-1	95-100	0-5	0
Am-241	0-1	95-100	0-5	0

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[1] The chemical decontamination methods utilizes cycled processes with alternating steps, in principle one acid step and one oxidation step. The abbreviations are names of different processes.

Theoretical background
The thermodynamic stability of different metallic oxides are most important as this will control if the metal will be oxidised or if will remain in solution in the steel. In general the reaction between a metal Me and oxygen may be described by the following reaction:

$$x \cdot Me + y \cdot O_2 \leftrightarrow Me_x O_{\frac{y}{2}}$$
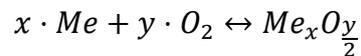
where x and y are the stoichiometric constant.

The Gibbs free energy (ΔG) of a reaction is a measure of the thermodynamic driving force that makes a reaction occur. A negative value for ΔG indicates that a reaction can proceed spontaneously without external inputs, while a positive value indicates that it will not. The equation for Gibbs free energy is:

$$\Delta G = \Delta H - T \square \Delta S$$

where ΔH is the enthalpy, T is absolute temperature, and ΔS is entropy.
The enthalpy (ΔH) is a measure of the actual energy that is liberated when the reaction occurs (the "heat of reaction"). If it is negative, then the reaction gives off energy, while if it is positive the reaction requires energy. The entropy (ΔS) is a measure of the change in the possibilities for disorder in the products compared to the reactants. For example, if a solid (an ordered state) reacts with a liquid (a somewhat less ordered state) to form a gas (a highly disordered state), there is normally a large positive change in the entropy for the reaction.

A simple way to compare the stability of different oxides is using an Ellingham diagram. Ellingham diagram is a plot of ΔG versus temperature. Since ΔH and ΔS are essentially constant with temperature unless a phase change occurs, the free energy versus temperature plot can be drawn as a series of straight lines, where ΔS is the slope and ΔH is the y-intercept. The slope of the line changes when any of the materials involved melt or vaporize. Free energy of formation is negative for most metal oxides, and so the diagram is drawn with ΔG=0 at the top of the diagram, and the values of ΔG shown are all negative numbers. One of the most common Ellingham diagram by metallurgists is shown in Figure 1. Temperatures where either the metal or oxide melt or vaporize are marked on the diagram. The Ellingham diagram shown is for metals reacting to form oxides (similar diagrams can also be drawn for metals reacting with sulphur, chlorine, etc., but the oxide form of the diagram is most common). The oxygen partial pressure is taken as 1 atmosphere, and all of the reactions are normalized to consume one mole of O_2.

In the figure the lines for the formation of cobalt oxide, zinc oxide and uranium oxide is marked together with the line of iron oxide. In general metals, which lines are below the iron line, can be oxides in steel melt and transferred to the slag. Reversed are metals, which are above the iron line, cannot be oxidised in liquid steel. Cobalt will stay in the steel melt as it seen from the figure that the cobalt oxide line is above the iron line. Similarly, uranium will be transferred to the slag as the uranium oxide line is below the iron oxide line. Zinc oxide is an example of an oxide that will vaporize from a liquid steel melt that is seen in the figure. The information found in the Ellingham diagram in agreement with the results presented in Table 1.

In Figure 2 a simplified Ellingham diagram is shown with lines for the heavy elements plutonium oxide and americium oxide together with iron oxide line. From this figure it is seen that both plutonium and americium forms stable oxides.
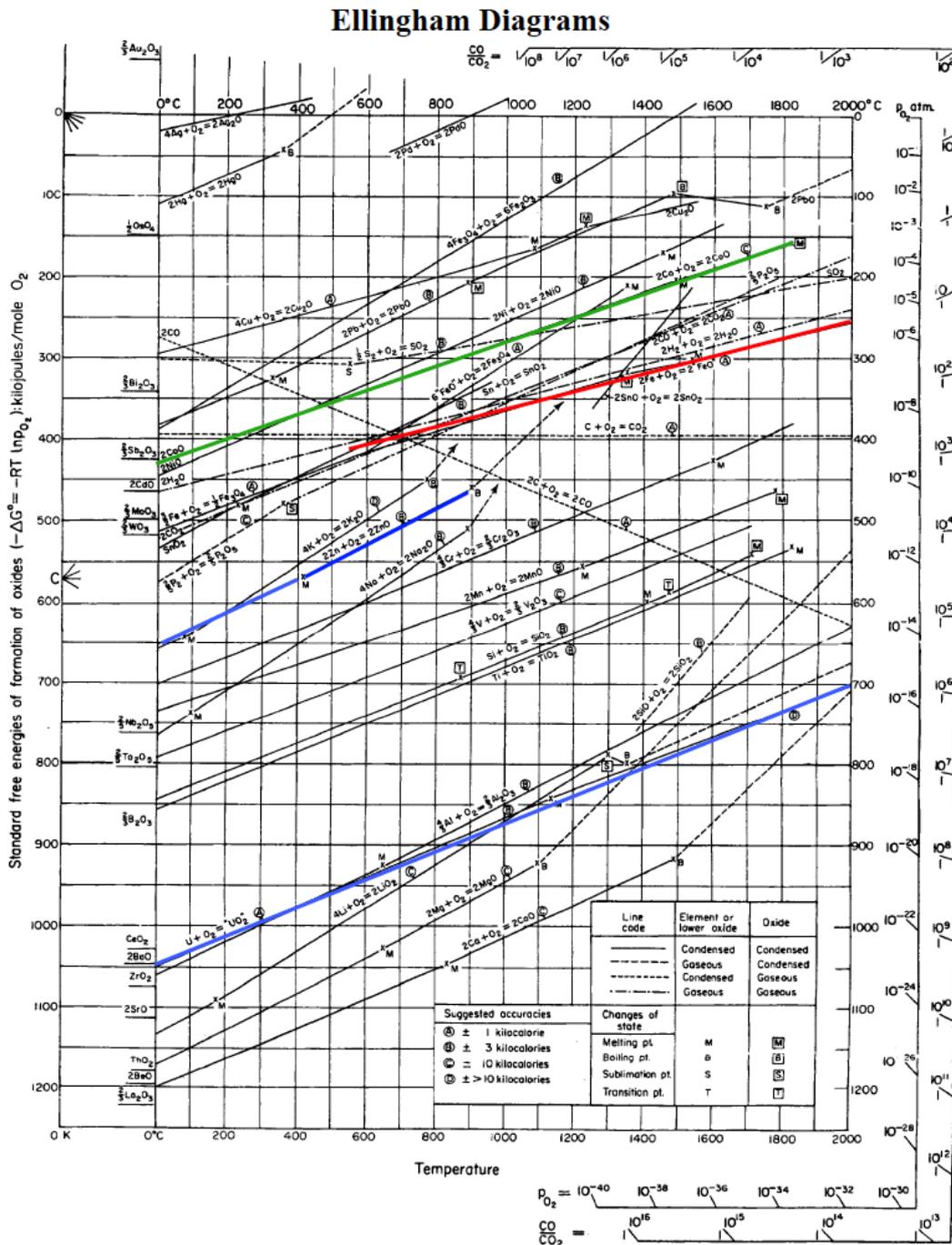
Figure 1
Typical Ellingham diagram for metallurgists.
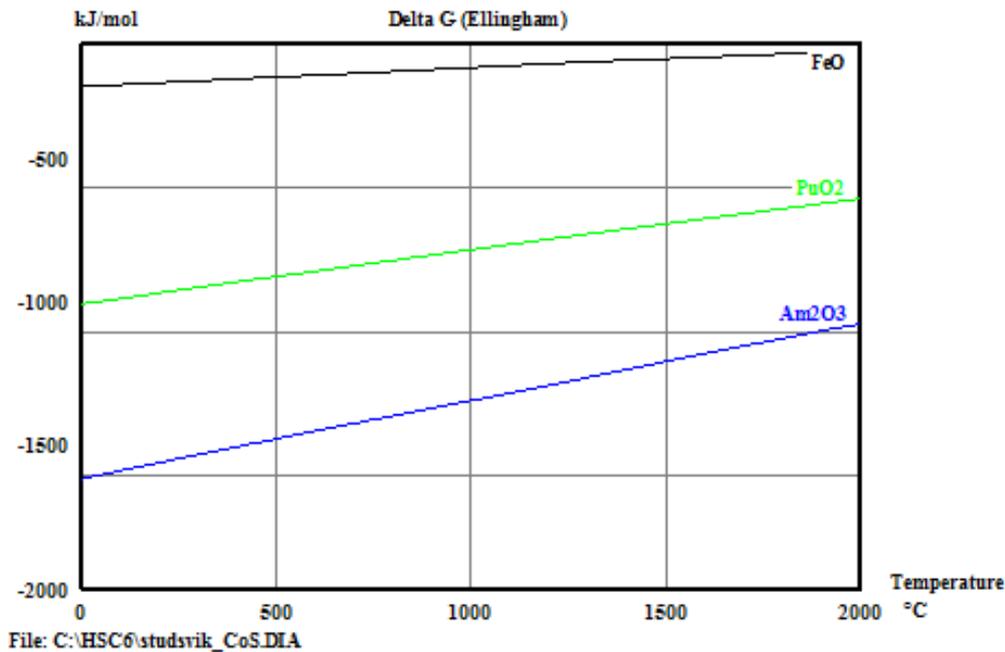
Figure 2
Simplified Ellingham diagram for plutonium oxide, americium oxide and iron oxide

Normal metallurgical refining processes
During normal scrape based steel production the scrape is first melted in an electric arc furnace (EAF) and tapped in a ladle. Through the melting in the EAF the steel will pickup oxygen from the atmosphere. This oxygen needs to be removed from the steel by additions of deoxidants usually aluminium or silicon. These agents are often added during tapping of the EAF and will form non-metallic inclusions, oxide particles, in the steel that also needs to be removed. The actual refining process is then preformed in a ladle station normally consisting of a ladle furnace (LF) and in many cases a degassing station. A schematic picture of a ladle station is shown in Figure 3. At the ladle station the slag from the EAF is removed and a synthetic slag is added to the ladle. This synthetic slag plays an important role in the refining process. The slag protects the liquid steel from oxidation from the atmosphere. The slag will also dissolve unwanted elements such as sulphur from the steel. Different stirring methods of the steel are employed during the ladle treatment to remove the inclusions. The stirring methods include both gas stirring and induction stirring and in some case a combination of the different methods. By using stirring and degassing, the levels of undesirable impurities such as sulphur reach low levels of 10-20 ppm.
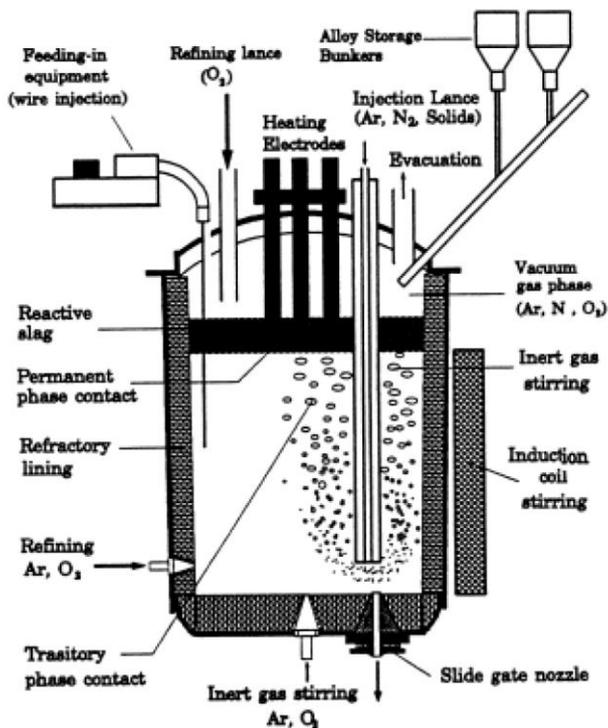
Figure 3
Schematic picture of a ladle station

Normal metallurgical refining processes for decontamination of steel scrape
The nuclides that will form more stable oxides then iron will probably give non-metallic inclusions in the liquid steel. This inclusion can then be removed using the normal stirring praxis's used in the steel industry combined with the addition of a suitable synthetic slag, slag former additions. However, this approach is not applicable to remove elements that have less stable oxides then iron.

Clearance, nuclides and amount of material

The level of separation needed depends on the nuclide as it is regulated by the competent authority through clearance limits, in some cases denoted free release or exemption.

Nuclides emitting high gamma radiation and alpha emitting nuclides have lower clearance limits than soft beta emitting nuclides and metals for remelting can in some cases have higher clearance limits than metals for direct re-use. In Sweden the clearance limits for un-conditional re-use is 0.1 Bq/g for Co-58, Co-60, Mn-54 and for Sr-90 and Sb-125 the clearance limit is 1 Bq/g and heavy elements such as Uranium, Americium and Plutonium vary between 0.01 and 10 Bq/g depending on the radiation emitted and the number of daughter nuclides.

A level of 1 Bq/g metal is not that many atoms, Table 2. Table 2 shown how many grams and atoms there are if the activity is 1Bq/g. As seen this is directly related to the half-life of the isotope.

Table 2
Number of grams and atoms in 1 Bq/g of certain isotopes

	T½ [s]	Grams of nuclide if 1 Bq/g	Atoms in 1 Bq/g
Mn-54	2.70E+07	3.50E-15	3.9E+07
Co-60	1.66E+08	2.39E-14	2.4E+08
Sr-90	9.06E+08	1.98E-13	1.3E+09
U-238	1.41E+17	8.06E-05	2.0E+17
Am-241	1.36E+10	8.06E-12	2.0E+10
Pu-238	2.77E+09	1.58E-12	4.0E+09

So separating so few atoms is a challenge and even if it can be done in theory is may still be a challenge in practice, in particular for isotopes that are not coming from corrosion of materials in a reactor system but are originating from the fuel, as fission products such as Sr-90.

Conclusions
Decontamination of steel from the nuclear industry can be done in-situ in the Nuclear Power Plant, or after the metal has been removed but not melted and in some cases also during melting. The choice of decontamination method is not oily governed by availability but also by the thermodynamic properties of the element of the radioactive isotope.

From thermodynamics it can be explained that Am, U, Pu as well as Zn is separated during melting, even if zinc may be in gaseous form. Thermodynamics also explain that Co-60, and all other radioactive cobalt isotopes, will stay in the molten metal when melted under standard conditions in air.

From an elemental perspective is the amount of a radioisotope very low in the melt which helps to understand that creating a synthetic slag, that specifically attracts these elements, in such a low concentration solution, i.e. molten metal, is not trivial.

However in the non-nuclear metals treatment industry the use of ladle furnaces synthetic slags and gas bubbling through the metal is widely used. This may be an opening for better separation of some elements, with radioisotopes, during melting in the future but more research is needed.

Reference
1   Nuclide Distribution in the Metal Recycling Process, P. Lidar, M. Lindberg, A. Larsson, and P. Konneus, Studsvik Nuclear AB 2014