

Exergy Analysis of Metal Oxide Carbothermic Reduction under Vacuum – Sustainability prospects

E. Balomenos*, D. Panias, I. Paspaliaris

National Technical University of Athens
Laboratory of Metallurgy
9, Heroon Polytechniou str., 157 73, Zographou Campus, Greece
* Corresponding author, email: thymis@metal.ntua.gr

Abstract

Based on the fundamental Le Chatellier principle, gas producing reactions can be pushed at lower temperatures if an appropriate vacuum is applied. A basic thermodynamic analysis is used to predict the effect of pressure decrease on the temperature and exergy cost of a reaction with gaseous products. The energy analysis of 11 different metal producing carbothermic reductions revealed that the pumping work substitutes relatively the same amount of heat in all 11 reactions, despite the fact that the volume of gases evolved in each case differs significantly. The exergy analysis for conducting these reactions with non-renewable resources showed that due to the high exergy cost of fossil fuel generated electricity the application of vacuum would increase the overall exergy cost of these reductions. If the heat needed for the reactions could be produced through renewable resources, such as concentrated solar radiation, then the use of vacuum would have a positive effect in the cases of high temperature reductions of Al_2O_3 , MgO and CaO , where a significant decrease in reaction temperature is observed as more exergy is spent in pumping work.

Keywords: Exergy, Vacuum Metallurgy, Carbothermic reduction, Solar furnaces

1. Introduction

Metallurgical processing under vacuum was firstly used during the first World War in Germany in order to degas and purify steel and nickel-chrome alloys (Kroll, 1951). Since then vacuum has been applied in processes

- requiring protection of a metal bath from oxidation, nitriding or from process produced gases (e.g. hydrogen)
- of metal purification and separation of alloys through selective volatilization of elements
- for dissociation of inorganic oxides which can undergo thermal decomposition in solid and gaseous components
- of metal oxide reductions from less volatile reducing agents (e.g. silicon or carbon), where the metal is usually produced in the gaseous phase and is recovered through condensation.

The latter two cases refer to metallurgical processes usually achievable at moderate or high temperatures under atmospheric pressure, which when conducted under vacuum can occur at significantly lower temperatures. This is due to the fundamental Le Chatellier principle which when applied in gas producing reactions, states that the extent of the reaction will be increased as the pressure is reduced. If these reactions take place at a temperature higher than that of the environment, then lowering the total pressure will result in lowering of the temperature needed for the reaction to occur. Practically this means that one can substitute part of the process heat needed for an endothermic reaction with pumping work and conduct the process at lower temperatures. While the overall energy needed for the reaction is not reduced, the prospect of utilizing concentrated solar radiation for providing process

heat (Murray, Steinfeld, Fletcher, 1995) has renewed interest in using vacuum as a way of reducing reaction's temperature to levels attainable in solar furnaces (Kruesi, Galvez, Halmann, Steinfeld, 2011). In the present paper a theoretical investigation of the exergy cost related to process heat and vacuum production is made for a group of characteristic metallurgical reactions.

2. Thermodynamic analysis

For any chemical reaction to occur an amount of enthalpy (ΔH), also known as heat of reaction, must be absorbed or released by the system in such conditions that the total chemical work of the system is negative or zero. The conditions mentioned refer to the intensive parameters of the system namely temperature, pressure and chemical potential. As known for a system under constant temperature and pressure its chemical work is expressed by the Gibbs free energy potential (ΔG) and the criteria for it being in a state of thermodynamic equilibrium is

$$\Delta G^{(T,P)} \leq 0 \quad (1)$$

The changes in the Gibbs free energy potential are connected with enthalpy and entropy changes in the system according to

$$\Delta G^{(T,P)} = \Delta H^{(T,P)} - T\Delta S^{(T,P)} \quad (2)$$

A reaction which at environmental conditions (T_0 , P_0) has a positive ΔH^0 and a positive ΔG^0 requires in order to take place the absorption of ΔH^0 Joules of heat which will be converted into ΔG^0 Joules of chemical work. Since this is essentially a heat transfer phenomenon, the temperature

of the heat reservoir supplying the ΔH^0 Joules of heat is crucial. Assuming that the thermodynamic functions ΔH and ΔS are practically invariant with temperature^a, then as the temperature rises the heat dissipation term $T\Delta S$ increases until the point where Eq. 1 is satisfied and the reaction takes place. Thus practically at T where $\Delta G^T=0$

$$\Delta G^0 - \Delta G^T = (\Delta H^0 - T_0\Delta S^0) - (\Delta H^T - T\Delta S^T) = \Delta S^0(T - T_0) \quad (3)$$

If the entropy change ΔS^0 is associated with a heat transfer of Q Joules at T temperature then

$$\Delta G^0 = (Q/T)(T - T_0) = Q(1 - T_0/T) \quad (4)$$

Eq. 4 is of course the maximum achievable work for a heat engine operating between the heat reservoirs T and $T_0 < T$. Thus depending on the choice of the standard reference states the Gibbs free energy potential of the system can be equated with the chemical exergy of the system (ΔE) [0], denoting the portion of the heat of the reaction $Q = \Delta H^0$ which will be utilized as chemical work, while the remaining $T_0\Delta S^0$ will be dissipated as irreversible heat (Q_{irr}). Thus

$$\Delta E = Q - Q_{irr} = \Delta H^0(1 - T_0/T) = \Delta G^0 = W_q \quad (5)$$

where W_q denotes the work that must be absorbed by the system through heating.

From Eq. 5 one can calculate the temperature of the heat reservoir supplying the heat of the reaction according to

$$T = T_0 / [1 - (\Delta E / \Delta H^0)] \quad (6)$$

The ratio $\lambda = \Delta E / \Delta H^0$ (slope of the exergy-enthalpy vector of the reaction) is a measure of the availability of energy of the reaction (Sato, 2004). The temperature calculated in Eq. 6 would be valid given the assumption mentioned earlier, that the enthalpy and entropy changes of the reaction are constant through-out the temperature region $T_0 - T$. It is therefore an approximation and not an exact calculation, but still useful for the discussion of the present work.

Returning to the case of a reaction with gaseous products which occurs at a pressure $P < P_0$, if one assumes that the pressure is reduced through an isothermal expansion of the gases (assumed to be ideal), then the work done against the atmospheric pressure is given by

$$W_p = n R T \ln(P_0/P) \quad (7)$$

where R is the universal gas constant, n is the total number of gaseous moles which undergo the isothermal expansion at temperature T .

During this isothermal expansion if no phase change occurs and therefore the internal energy of the system remains constant, in accordance with the first law of thermodynamics, all the work described in Eq. 7 will be

^a This implies that no phase changes occur as the temperature increases and that C_p coefficients of reactants and products are invariant of temperature. The first assumption would be true if one chooses correctly the phases of the reactants at (T_0, P_0) and the phases of the products at (T, P) where the reaction takes place. The second assumption is obviously false; however the temperature dependence of the C_p coefficients is usually small and therefore can be omitted in a "crude" approximation.

converted to heat dissipated in the system. This is equivalent with stating that the work done to the system is used to increase the entropy related to the compressible phases of the system, as they can now occupy more space at the same temperature. Thus one can define the entropy increase due to pumping,

$$\Delta S_p = Q_p/T = W_p/T = n R \ln(P_0/P) \quad (8)$$

Returning to equation (3), the exergy change of the system undergoing a chemical reaction from an initial state (T_0, P_0) to the final state (T, P) is given by

$$\Delta E^* = \Delta H^0 - Q_{irr} - W_p = W_q^* \quad (9)$$

The heat of reaction ΔH^0 remains the same as it reflects the total energy needed to change the reactants into products. Likewise the irreversible heat losses Q_{irr} which are linked with the entropy change associated with the transformation of the reactants into products at (T_0, P_0) will remain the same. Thus the pressure decrease reduces directly the exergy change (ΔE) associated with the reaction or the work that must be absorbed by the system through heating for the reaction to take place. Additionally, according to Eq. 6 the temperature at which this heating has to take place is reduced to $T^* < T$.

Therefore when conducting an endothermic gas evolving reaction one can be more resource efficient if the sum of exergy spent in pumping (W_p) and in producing heat at T^* ($W_q + Q_{irr}$) is less than the exergy spent in producing all the heat of the reaction (Q) at $T > T^*$.

3. Carbothermic Reduction of metal oxides under vacuum

A field where resource efficiency is of the utmost importance is the extractive metallurgy related with metal production from metal oxides. Oxides like hematite (Fe_2O_3), alumina (Al_2O_3), magnesia (MgO) or even water (H_2O) can be reduced by carbon, yielding elemental phases and CO gases, according to the general reaction



Utilizing the Factsage 6.1 Software the enthalpy, entropy and Gibbs free energy potential changes are calculated for the carbothermic reduction of different oxides at environmental conditions (298.15 K, 1 atm) as well as at lower pressures and are presented in the first five columns of Table 1. Based on these figures the irreversible heat losses $Q_{irr}^{(T_0, P_0)} = T_0\Delta S^0$ (where $T_0 = 298.15$ K and $P_0 = 1$ atm) are calculated in column 6 while the ratio λ and the temperature T of the heat reservoir needed to provide the heat of the reaction (Eq. 6) are calculated in columns seven and eight. The final state of the produced metal was calculated based on temperature T and pressure P . On the ninth column of Table 1 the pumping work to achieve pressure P at temperature T is calculated according to Eq. 7. On the final column the work that must be absorbed by the system through heating (W_q) at temperature T and pressure P is calculated based on Eq. 9 (column 2 minus the summation of columns 6 and 9).

The effect of pressure decrease on the reaction temperature calculated in Table 1 is shown for all reactions considered in Figure 1.

As seen in Figure 1, these type of reactions under vacuum, can be separated according to their respective temperature regions, into high temperature carbothermic reductions (Al, Ca, Mg), moderate temperature carbothermic reductions (Na, Zn, Sn, Ge, Fe) and low temperature carbothermic reductions (Ni, H₂, Pb). The pressure dependence of ΔH , ΔG , W_p and W_q , as described

in Table 1, for one element from each group, namely aluminium, iron and hydrogen, are shown in Figures 2 to 4. In Figures 5 to 7 the relevant energy distribution for the three reactions are shown, along with the total heat needed at temperature of the reaction $Q(T) = W_q(T) + Q_{irr}$.

Table 1: Carbothermic Reduction of Metal oxides. All values are given per kg of produced metal. (*Note: At $T=2347$ K and $P=1$ atm the produced Aluminum would be liquid rather than gaseous, however in order to have a uniform base for comparisons, a hypothetical gaseous final state was chosen, as at lower pressures Aluminum is gaseous).

T_0	P	$\Delta H^{(T_0,P)}$	$\Delta G^{(T_0,P)}$	$\Delta S^{(T_0,P)}$	$Q_{irr}^{(T_0,P_0)}$	$\lambda=\Delta G/\Delta H$	T	$W_p^{(T,P)}$	$W_q^{(T,P)}$
K	Atm	MJ	MJ	MJ/K	MJ		K	MJ	MJ
$Al_2O_3(s) + 3C(s) = 2Al(g) + 3CO(g)^*$									
298.15	1.00E+00	37.128	32.412	0.016	4.716	0.87	2347.44	0.000	32.412
298.15	1.00E-01	37.128	31.883	0.018	4.716	0.86	2110.71	3.744	28.668
298.15	1.00E-02	37.128	31.354	0.019	4.716	0.84	1917.35	6.802	25.610
298.15	1.00E-03	37.128	30.826	0.021	4.716	0.83	1756.47	9.347	23.065
298.15	1.00E-04	37.128	30.297	0.023	4.716	0.82	1620.47	11.497	20.915
298.15	1.00E-05	37.128	29.768	0.025	4.716	0.80	1504.02	13.339	19.073
$Fe_2O_3(s) + 3C(s) = 2Fe(s) + 3CO(g)$									
298.15	1.00E+00	4.425	2.977	0.005	1.448	0.67	911.40	0.000	2.977
298.15	1.00E-01	4.425	2.824	0.005	1.448	0.64	824.12	0.424	2.554
298.15	1.00E-02	4.425	2.671	0.006	1.448	0.60	752.10	0.773	2.204
298.15	1.00E-03	4.425	2.517	0.006	1.448	0.57	691.65	1.067	1.910
298.15	1.00E-04	4.425	2.364	0.007	1.448	0.53	640.20	1.317	1.660
298.15	1.00E-05	4.425	2.211	0.007	1.448	0.50	595.87	1.532	1.445
$MgO(s) + C(s) = Mg(g) + CO(g)$									
298.15	1.00E+00	26.253	22.408	0.013	3.844	0.85	2036.06	0.000	22.408
298.15	1.00E-01	26.253	21.939	0.014	3.844	0.84	1814.35	2.858	19.550
298.15	1.00E-02	26.253	21.469	0.016	3.844	0.82	1636.20	5.155	17.253
298.15	1.00E-03	26.253	20.999	0.018	3.844	0.80	1489.92	7.041	15.367
298.15	1.00E-04	26.253	20.530	0.019	3.844	0.78	1367.64	8.618	13.790
298.15	1.00E-05	26.253	20.060	0.021	3.844	0.76	1263.91	9.955	12.453
$GeO_2(s) + 2C(s) = Ge(s) + 2CO(g)$									
298.15	1.00E+00	4.944	3.405	0.005	1.539	0.69	957.78	0.000	3.405
298.15	1.00E-01	4.944	3.248	0.006	1.539	0.66	869.02	0.458	2.947
298.15	1.00E-02	4.944	3.091	0.006	1.539	0.63	795.36	0.838	2.567
298.15	1.00E-03	4.944	2.934	0.007	1.539	0.59	733.17	1.159	2.246
298.15	1.00E-04	4.944	2.777	0.007	1.539	0.56	680.04	1.434	1.971
298.15	1.00E-05	4.944	2.619	0.008	1.539	0.53	634.05	1.671	1.734
$H_2O(l) + C(s) = H_2(g) + CO(g)$									
298.15	1.00E+00	86.961	49.627	0.125	37.334	0.57	694.48	0.000	49.627
298.15	1.00E-01	86.962	43.965	0.144	37.334	0.51	603.02	11.499	38.129
298.15	1.00E-02	86.962	38.302	0.163	37.334	0.44	532.84	20.321	29.307
298.15	1.00E-03	86.962	32.639	0.182	37.334	0.38	477.29	27.304	22.324
298.15	1.00E-04	86.962	26.976	0.201	37.334	0.31	432.23	32.969	16.660
298.15	1.00E-05	86.962	21.313	0.220	37.334	0.25	394.94	37.656	11.972

Table 1 (Continued): Carbothermic Reduction of Metal oxides. All values are given per kg of produced metal. (*Note: At $T=2347\text{ K}$ and $P = 1\text{ atm}$ the produced Aluminum would be liquid rather than gaseous, however in order to have a uniform base for comparisons, a hypothetical gaseous final state was chosen, as at lower pressures Aluminum is gaseous).

T_0	P	$\Delta H^{(T_0,P)}$	$\Delta G^{(T_0,P)}$	$\Delta S^{(T_0,P)}$	$Q_{irr}^{(T_0,P_0)}$	$\lambda = \Delta G / \Delta H$	T	$W_p^{(T,P)}$	$W_q^{(T,P)}$
K	Atm	MJ	MJ	MJ/K	MJ		K	MJ	MJ
$ZnO(l) + C(s) = Zn(g) + CO(g)$									
298.15	1.00E+00	4.833	3.534	0.004	1.299	0.73	1109.21	0.000	3.534
298.15	1.00E-01	4.833	3.359	0.005	1.299	0.70	977.79	0.573	2.961
298.15	1.00E-02	4.833	3.185	0.006	1.299	0.66	874.21	1.024	2.510
298.15	1.00E-03	4.833	3.010	0.006	1.299	0.62	790.47	1.389	2.145
298.15	1.00E-04	4.833	2.835	0.007	1.299	0.59	721.37	1.690	1.844
298.15	1.00E-05	4.833	2.661	0.007	1.299	0.55	663.38	1.943	1.591
$Na_2O(s) + C(s) = 2Na(g) + CO(g)$									
298.15	1.00E+00	11.354	8.606	0.009	2.748	0.76	1231.66	0.000	8.606
298.15	1.00E-01	11.354	8.233	0.010	2.748	0.73	1084.70	1.355	7.251
298.15	1.00E-02	11.354	7.861	0.012	2.748	0.69	969.06	2.421	6.185
298.15	1.00E-03	11.354	7.488	0.013	2.748	0.66	875.71	3.282	5.324
298.15	1.00E-04	11.354	7.116	0.014	2.748	0.63	798.76	3.991	4.615
298.15	1.00E-05	11.354	6.744	0.015	2.748	0.59	734.23	4.586	4.020
$NiO(s) + C(s) = Ni(s) + CO(g)$									
298.15	1.00E+00	2.210	1.271	0.003	0.939	0.58	701.63	0.000	1.271
298.15	1.00E-01	2.210	1.174	0.003	0.939	0.53	635.83	0.207	1.064
298.15	1.00E-02	2.210	1.077	0.004	0.939	0.49	581.26	0.379	0.892
298.15	1.00E-03	2.210	0.979	0.004	0.939	0.44	535.36	0.524	0.747
298.15	1.00E-04	2.210	0.882	0.004	0.939	0.40	496.14	0.647	0.624
298.15	1.00E-05	2.210	0.785	0.005	0.939	0.36	462.31	0.754	0.517
$CaO(s) + C(s) = Ca(g) + CO(g)$									
298.15	1.00E+00	17.525	15.227	0.008	2.298	0.87	2274.23	0.000	15.227
298.15	1.00E-01	17.525	14.943	0.009	2.298	0.85	2023.34	1.933	13.294
298.15	1.00E-02	17.525	14.658	0.010	2.298	0.84	1822.36	3.482	11.746
298.15	1.00E-03	17.525	14.373	0.011	2.298	0.82	1657.70	4.751	10.476
298.15	1.00E-04	17.525	14.088	0.012	2.298	0.80	1520.29	5.810	9.418
298.15	1.00E-05	17.525	13.803	0.012	2.298	0.79	1403.95	6.706	8.521
$PbO(s) + C(s) = Pb(s) + CO(g)$									
298.15	1.00E+00	0.527	0.253	0.001	0.273	0.48	574.37	0.000	0.253
298.15	1.00E-01	0.527	0.226	0.001	0.273	0.43	521.69	0.048	0.205
298.15	1.00E-02	0.527	0.198	0.001	0.273	0.38	478.00	0.088	0.165
298.15	1.00E-03	0.527	0.171	0.001	0.273	0.32	441.07	0.122	0.131
298.15	1.00E-04	0.527	0.143	0.001	0.273	0.27	409.43	0.151	0.102
298.15	1.00E-05	0.527	0.116	0.001	0.273	0.22	382.03	0.176	0.077
$SnO_2(s) + C(s) = Sn(l) + CO(g)$									
298.15	1.00E+00	3.083	2.093	0.003	0.990	0.68	928.30	0.000	2.093
298.15	1.00E-01	3.083	1.997	0.004	0.990	0.65	846.17	0.273	1.820
298.15	1.00E-02	3.083	1.900	0.004	0.990	0.62	777.32	0.501	1.591
298.15	1.00E-03	3.083	1.804	0.004	0.990	0.59	718.89	0.696	1.397
298.15	1.00E-04	3.083	1.708	0.005	0.990	0.55	668.59	0.863	1.230
298.15	1.00E-05	3.083	1.612	0.005	0.990	0.52	624.86	1.008	1.085

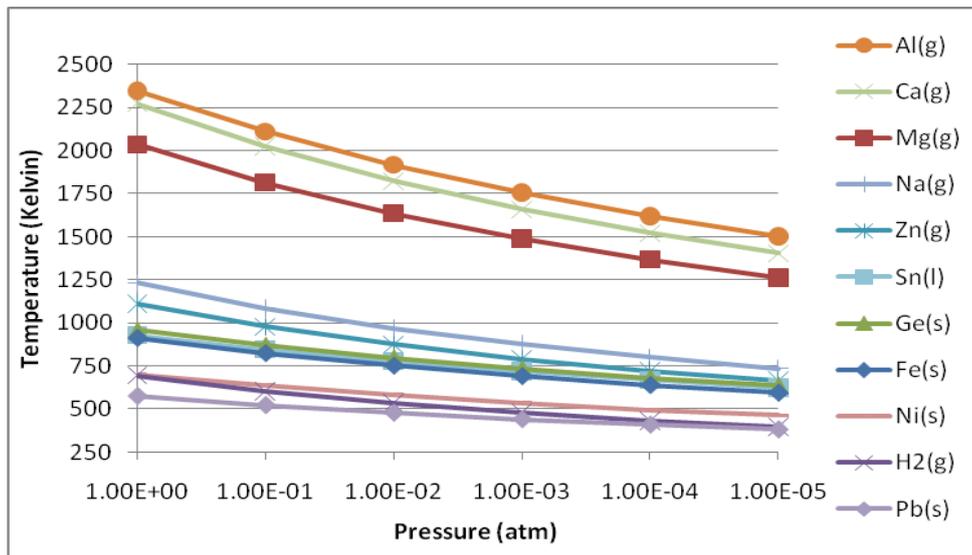


Figure 1: Temperatures of metal producing carbothermic reactions as described in Table 1.

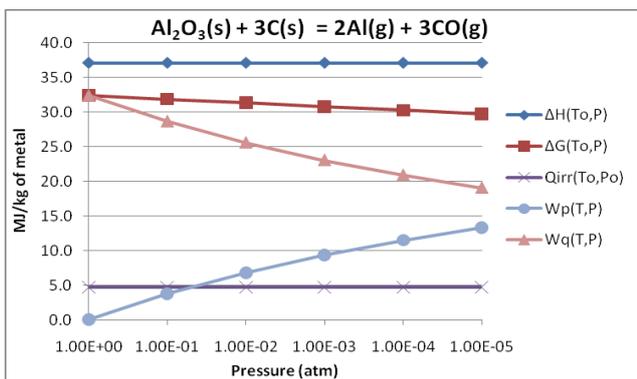


Figure 2: Pressure dependance of thermodynamic functions and ideally required work for the carbothermic reduction of Al_2O_3 .

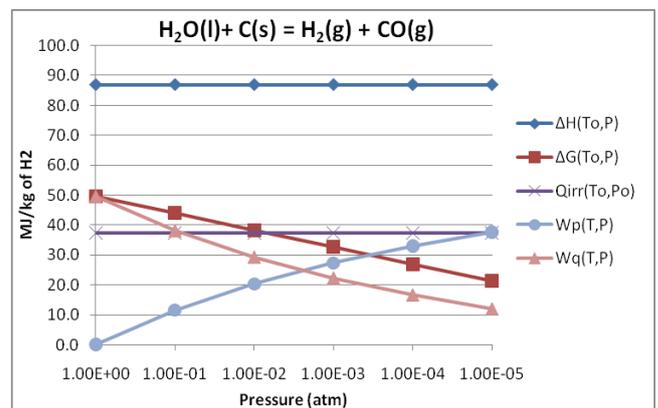


Figure 4: Pressure dependance of thermodynamic functions and ideally required work for the carbothermic reduction of H_2O .

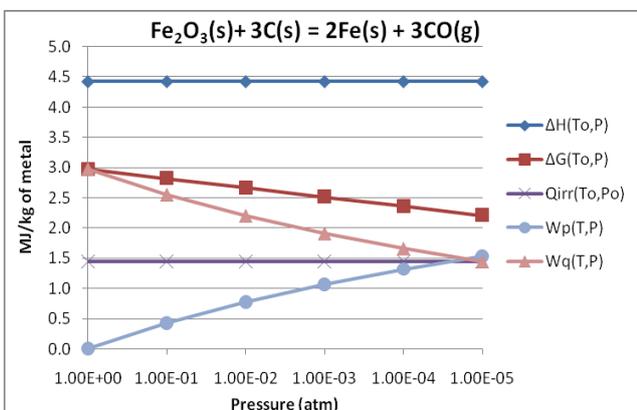


Figure 3: Pressure dependance of thermodynamic functions and ideally required work for the carbothermic reduction of Fe_2O_3 .

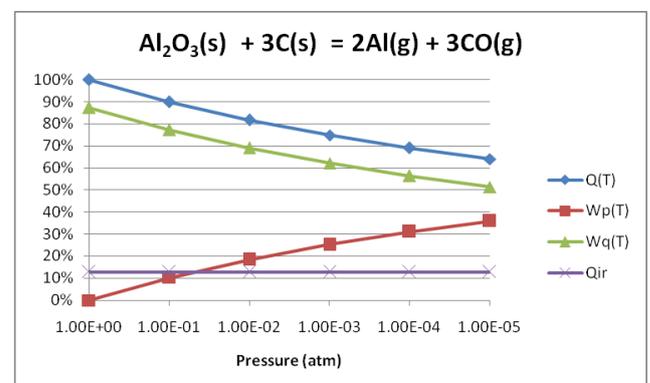


Figure 5: Pressure dependance of the ideal pumping work, chemical work, irreversible heat losses and total heat required in relation to reaction ΔH° at atmospheric pressure, for the carbothermic reduction of Al_2O_3 .

From Figures 2 to 7 it is evident that as the temperature region of the carbothermic reduction is lowered (from Al to H_2) the effect of the irreversible heat losses at T_0 (Q_{irr}) becomes important, while the total effect of the pumping work is more or less similar in all cases despite the fact that different amount of gases are evolved in each case. The

latter is verified in Figure 8 where the percentage of pumping work relative the whole energy required for the reaction (ΔH°) is presented for all carbothermic reductions considered.

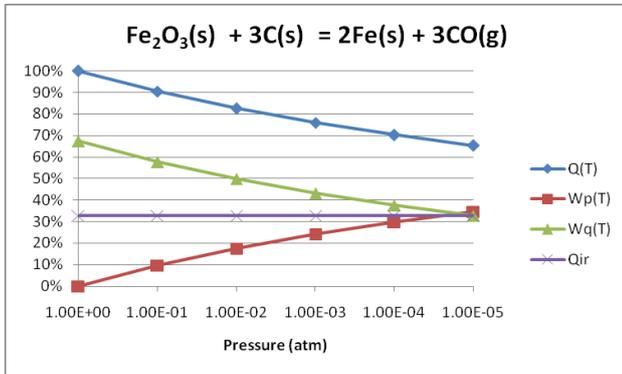


Figure 6: Pressure dependence of the ideal pumping work, chemical work, irreversible heat losses and total heat required in relation to reaction ΔH° at atmospheric pressure, for the carbothermic reduction of Fe_2O_3 .

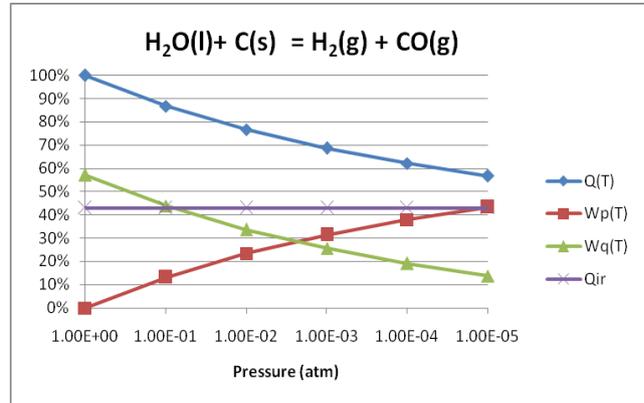


Figure 7: Pressure dependence of the ideal pumping work, chemical work, irreversible heat losses and total heat required in relation to reaction ΔH° at atmospheric pressure, for the carbothermic reduction of H_2O

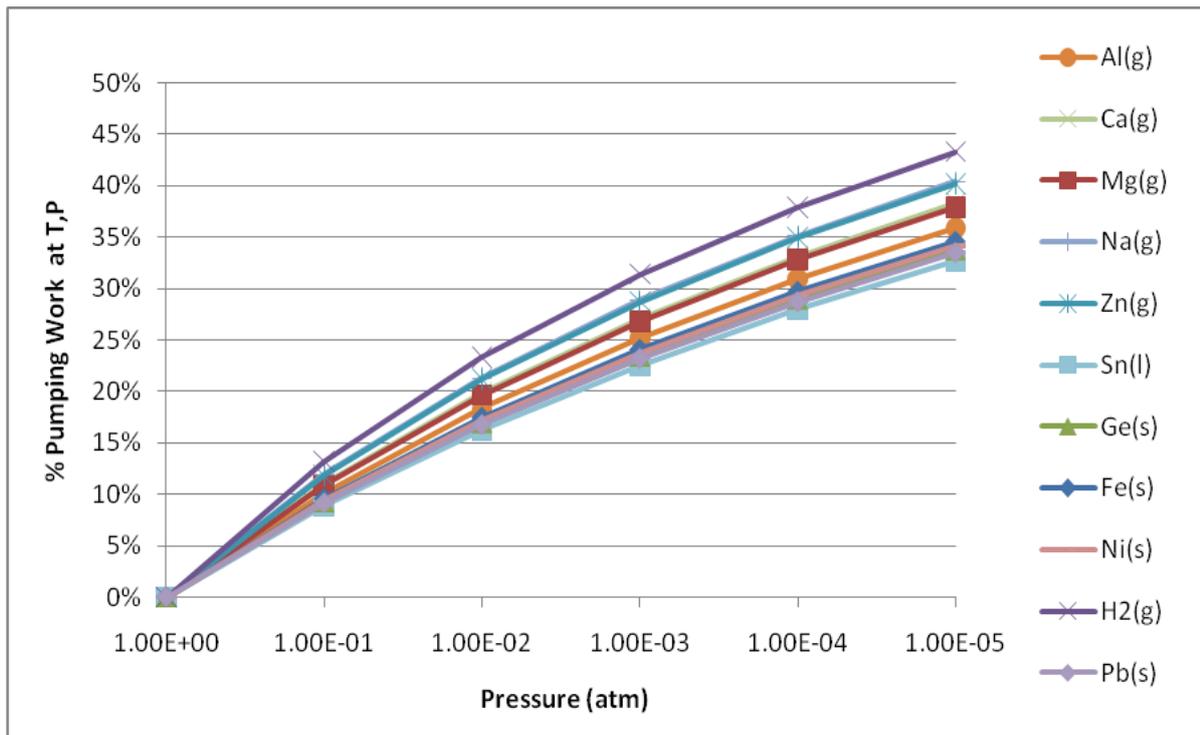


Figure 8: Relative pumping work needed for different metal production through carbothermic reduction under different pressures according to data of Table 1.

To assess the potential resource efficiency from conducting these reactions under vacuum it is now necessary to examine the exergy cost related with producing the needed pumping work W_p and the overall heat supply ($Q(T) = W_q(T) + Q_{irr}$). The pumping work industrially is produced through electrical (for the most part) or diesel burning vacuum pumps. Heating can be provided either through electric furnaces (resistance furnaces, inductive furnaces or Electric arc furnaces) through fossil fuel burning furnaces (calciners, rotary kilns, blast furnaces) or through solar furnaces utilizing concentrated solar radiation. Assuming all machines to be ideal (or to suffer from the same degree of imperfection) and disregarding diesel powered vacuum pumps which would be unsuitable for large scale industrial production, a comparison can be made between utilizing electrically powered vacuum pumps with different types of furnaces. Obviously the comparison of electrical pumping work coupled with electrical heating is pointless as the machines

are assumed ideal and therefore the total sum of exergy spent is constantly the same. The same is not true when comparing a fossil fuel burning furnace coupled to an electrical vacuum pump. The electricity powering the vacuum pump is assumed to be produced in a fossil fuel burning power plant, utilizing the same fossil fuel as the above mentioned furnace. When this fossil fuel is coal, with a chemical exergy of 34.10 MJ/kg^b , in the coal burning furnace it can be transformed fully into process heat while in the power plant it can be transformed only partially to electricity. Assuming an overall 40% thermal efficiency for transforming coal exergy to electricity, the exergy cost, calculated in kilograms of required coal, for the carbothermic reduction of alumina, hematite and water under different pressures are presented in Figures 9 to 11.

^b The chemical exergy of coal is here equated with its Higher Heating Value (HHV) (Brodyansky, 1994)

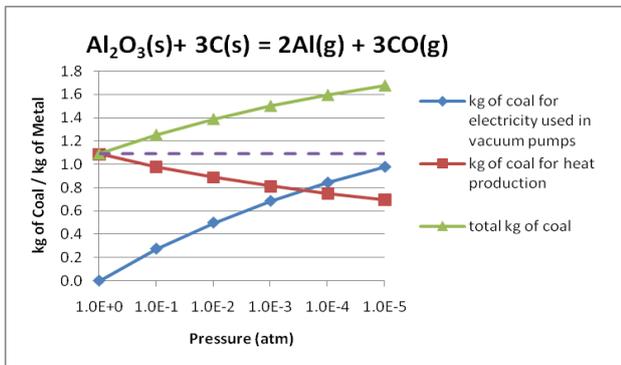


Figure 9: Exergy costs measured in kg of coal needed for process heating and electricity generation per kg of metal produced for the carbothermic reduction of Al_2O_3 , under different pressures. The dashed line shows the kg of coal needed for providing enough process

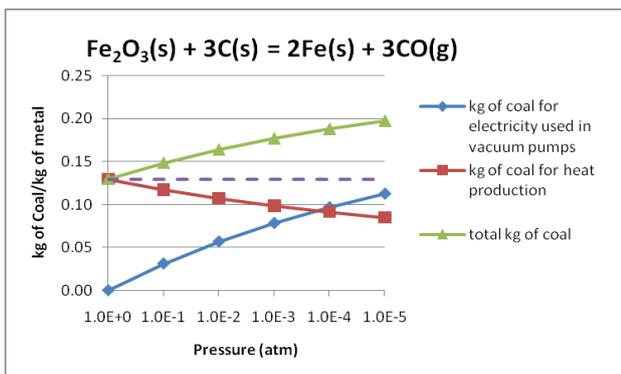


Figure 10: Exergy costs measured in kg of coal needed for process heating and electricity generation per kg of metal produced for the carbothermic reduction of Fe_2O_3 under different pressures. The dashed line shows the kg of coal needed for providing enough process

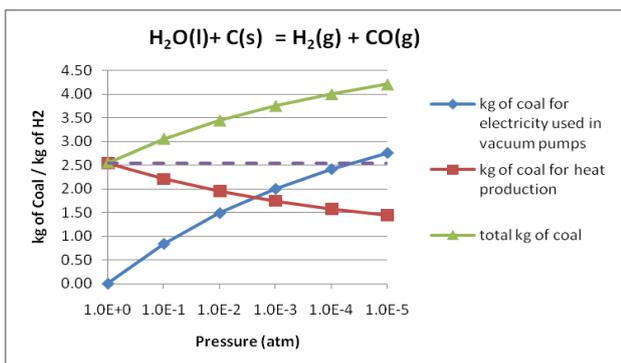


Figure 11: Exergy costs measured in kg of coal needed for process heating and electricity generation per kg of metal produced for the carbothermic reduction of H_2O under different pressures. The dashed line shows the kg of coal needed for providing enough process heat for the carbothermic reduction to take place at atmospheric pressure.

As expected in all cases the total exergy/resource cost for producing heat and vacuum is higher than the cost of producing the heat of reaction at atmospheric pressure (dashed lines in Figures 9-11). However based on these figures it is possible to estimate the potential of utilizing solar furnaces coupled with the electrically powered vacuum pumps, thereby providing heat through renewable sources and reducing the resource cost to that of powering only the vacuum pumps. If the later exergy cost (as kg of

coal needed for their electricity) is less than the exergy cost needed to provide the heat of reaction at atmospheric pressure through non-renewable sources (e.g. coal) then the process is more resource efficient. In Figure 12 the relative exergy cost of the pumping work (kg of coal for ΔH° heat at T_o, P_o) is presented for all reactions considered, while in Figure 13 this exergy cost is plotted against the temperature that must be achieved in the solar furnace for the reaction to take place under the relative vacuum.

As seen in Figure 12 at low pressures ($P < 10^{-5}$ atm) the exergy gains from utilizing solar furnaces are relatively small (20% or less), but on the other hand as seen in Figure 13 for the high temperatures carbothermic reductions (Al, Ca, Mg) the reduction in the temperature of furnace operation is quite large. The same is not true for the moderate and low temperature carbothermic reductions, where the exergy spent for vacuum has a much smaller effect in the reaction temperature decrease and it would be theoretically better to simply supply all the reaction heat needed at atmospheric pressure.

4. Conclusions

A basic thermodynamic analysis can be used to predict the effect of pressure decrease on the temperature and exergy cost of a reaction with gaseous products. Such reactions with significant industrial interest are the carbothermic reductions of metal oxides, which can be divided into high, moderate and low temperature reductions based on the relative reaction temperature. The energy analysis of 11 different metal producing carbothermic reductions revealed that the pumping work substitutes relatively the same amount of heat in all 11 reactions, despite the fact that the volume of gases evolved in each case differs significantly. The exergy analysis for conducting these reactions with non-renewable resources showed that due to the high exergy cost of fossil fuel generated electricity the application of vacuum would increase the overall exergy cost of these reductions. On the other hand, if the heat needed for the reactions could be produced through renewable resources, such as concentrated solar radiation, then the use of vacuum would have a positive effect in the cases of high temperature reductions where a significant decrease in reaction temperature is observed as more exergy is spent in pumping work. Therefore one could conclude that vacuum metallurgy has a potential of being coupled with future solar furnace technology in a effort primarily to limit the temperature of operation for high temperature reactions. If for example a vacuum between 10^{-3} to 10^{-4} atm is applied then the carbothermic reduction of Al_2O_3 , CaO and MgO can be achieved at temperatures between 1750 to 1500 K with a total exergy cost of 60% to 80% of the total reaction enthalpy. However, under ideal conditions and maximum efficiency for concentrating solar radiation, one would need a mean solar flux concentrations of 5000 suns to achieve 1500 K and 10000 suns to achieve 1700 K (Steinfeld and Palumbo, 2001). Modern day solar tower facilities can achieve concentrations between 500 to 5000 suns, while solar dish systems can achieve concentration between 1000 to 10000 suns. Thus while it is theoretically possible to achieve such temperatures and perform high temperature reductions at lower exergy cost by utilizing solar radiation it is obvious that in practice this can only be achieved at the limit of the current state-of-the-art solar technology.

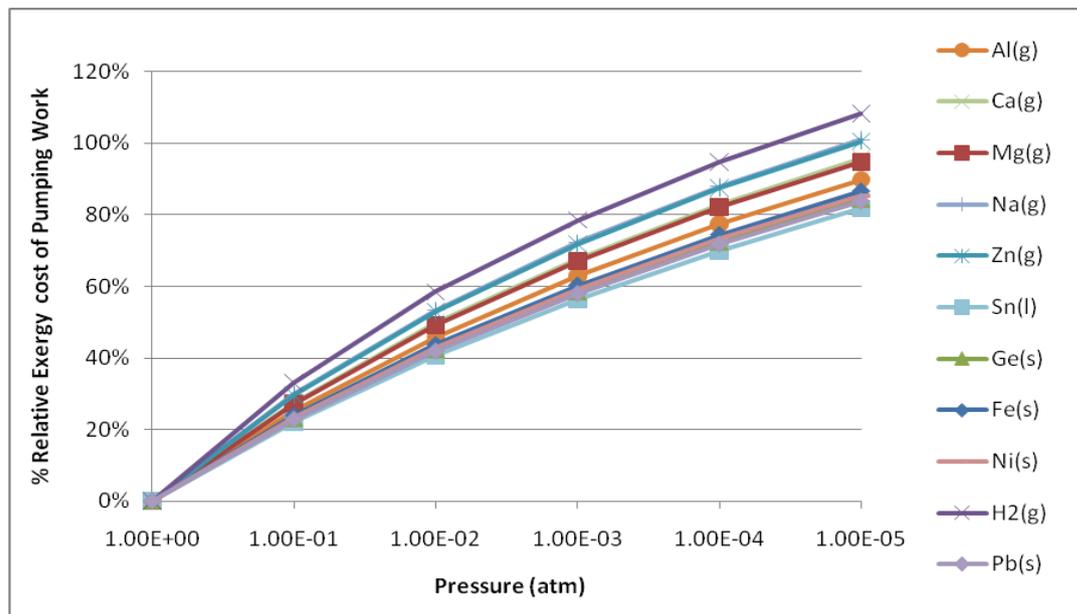


Figure 12: Exergy cost of pumping work relative to the total energy requirement of the reaction (ΔH^0) for all the carbothermic reductions considered in Table 1.

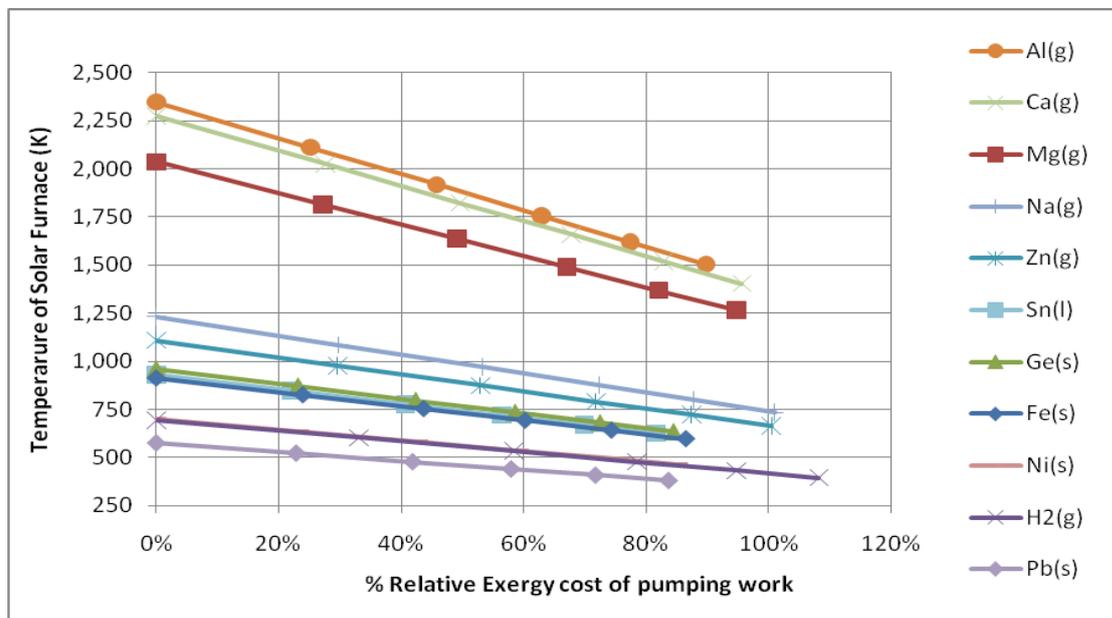


Figure 13: Reaction temperature decrease in relation to the relative exergy cost of pumping work (Figure 6) needed for all the carbothermic reductions considered in Table 1.

Acknowledgements

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n° ENER/FP7EN/249710/ENEXAL.

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