

THERMODYNAMIC STUDY OF NO_x AND SO₂ FORMATION AND POSSIBLE REDUCTION DURING Pb WASTE RECYCLING

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Professional paper
Received: May 13th, 2020
Accepted: June 29th, 2020
HAE-1962

<https://doi.org/10.33765/thate.11.3.2>

ABSTRACT

With the increasing demand for electricity due to the increasing economic boom, there is an excessive production of emissions that natural processes cannot cope with. Fortunately, there are various technological solutions for capturing harmful substances from produced emissions. However, the European Union aims to prevent the formation of emissions in the process of industrial production itself. In order to achieve this, it is necessary to reconcile the interests of individual European Union member states by the implementation of regulations into laws, to monitor short-term and long-term changes in air quality, and also to put into practice increasingly effective methods of capturing emissions from the air. This paper offers an example of thermodynamic calculation of quantities by appropriate software in the process of recycling waste from the metallurgical industry and possibilities of technological improvement in emission reduction.

Keywords: *air quality, SO₂ emissions, NO_x emissions, lead accumulators, HSC chemistry 6.1*

INTRODUCTION

The annual increase in energy demand and consumption forces power plants to produce more and more electricity and heat. Consequently, it also increases the production of more polluting gases, especially in urban areas. In the production of thermal energy, the combustion of fossil fuels produces harmful gaseous chemical compounds, such as carbon dioxide (CO₂), sulphur dioxide (SO₂), nitrogen oxides (NO_x), unburnt hydrocarbons (UHCs), as well as solid particles. Road transport also

accounts for a significant proportion, accounting for almost 60 % of emissions in the European Union (EU).

SO₂ and NO_x belong to the gaseous pollutants produced by the combustion of fossil fuels. With secondary pollutants derived from SO₂ and NO_x, such as sulphuric acid (H₂SO₄), nitric acid (HNO₃), they are harmful to humans and the natural environment [1]. Acid rains containing weak sulphuric and nitric acids enter the soil, leaching out elements such as calcium, manganese, sodium, potassium,

which significantly deteriorates its quality and consequently the quality of watercourses. As a result of insufficient water supply, trees in forests dry up and die. The adverse effect of acid rains is also reflected in buildings, erosion of statues and corrosion of metal structures. That is why the issue of SO₂ and NO_x emissions is still very topical - one of the critical problems in pollution control and air quality management.

The European Pollutant Release and Transfer Register (E-PRTR) covers the 27 EU member states as well as Iceland, Lichtenstein, Norway, Serbia, and Switzerland. The E-PRTR contains data reported from approximately 30,000 industrial installations per year, 65,000 different economic activities, including nine industrial sectors: energy, metal production and processing, metallurgical and chemical industries, waste and wastewater management, paper and wood-processing industries, meat and livestock production, agriculture and other activities [2]. The data from the register is processed into an interactive map of European countries in Figure 1, which provides information on air quality based on the European Air Quality Index. The European Air Quality Index shows the status of short-term air quality at each of over 2,000 monitoring stations across Europe. The index consists of an interactive map of local air quality by measuring stations based on five key pollutants that harm human health and the environment: particulate matter (PM_{2.5} and PM₁₀), ground-level ozone (O₃), nitrogen dioxide (NO₂) and sulphur dioxide (SO₂). European Union legislation sets air quality standards for short (hourly/daily) and long (annual) periods. Therefore, the index does not reflect the long-term (annual) air quality situation, which may vary significantly [3].

Circles on the map represent the locations of air quality monitoring stations. Based on data from the interactive map, air quality in most of Europe is good. Less satisfactory results are from the southern part of Europe, where air quality is moderate to poor. Good air quality is achieved when the concentration of the five measured pollutants, such as particle matters PM_{2.5} and PM₁₀, and NO₂, O₃ and SO₂ are

ranging between 0 to 10, 20, 40, 50, 100 µg/m³, respectively [3].

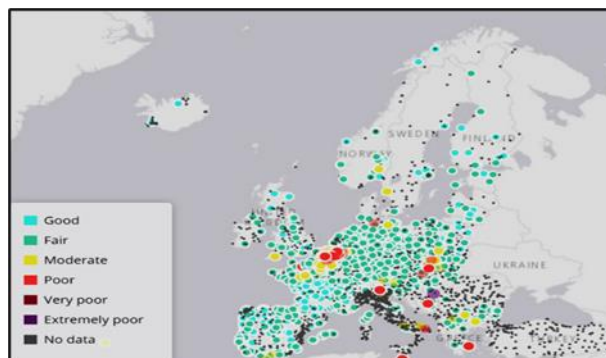


Figure 1. Current air quality (20 April 2020, 12:00 h) across all cities based on the European Air Quality Index [3]

The Copernicus Atmosphere Monitoring Service (CAMS) provides continuous information on atmospheric composition values in Europe and worldwide [4]. The service analyses the current situation forecasts for the next days, and also shows a look back into the past on air quality and atmospheric composition, ozone and UV radiation, emissions, climate change and solar radiation. The output is, for example, an interactive map of changes in the concentration of ozone, nitrogen and sulphur oxides, carbon monoxide, particle matters PM₁₀ and PM_{2.5} or secondary inorganic aerosols on the surface of the earth or 500 - 3000 m above the surface in µg/m³. The information about pollution could be viewed in time scale 24 hours before real-time and provides the air quality forecast for the next 96 hours. The output can be also a report on the air condition, which can be generated after registration on the service page with feedback for 30 days. From Figure 2 it is evident that in 2017 the most greenhouse gases in the European Union were produced by Luxembourg (20 t/person/year) and the least by Lichtenstein (5.1 t/person/year) [5].

NO_x and SO₂ emissions can potentially occur during the hydrometallurgical processing of raw materials/intermediates to obtain useful metals. These may be intermediate products resulting from the processing of various metal-containing ores, e.g., sulphide concentrates of metals [6]. They also occur, for example, in

the recycling of electrical and electronic waste or in the recycling of lead-acid batteries, where leaching of stone and slag (lead melting intermediates) in nitric and sulfuric acid produces NO_x or SO₂ emissions [6, 7].

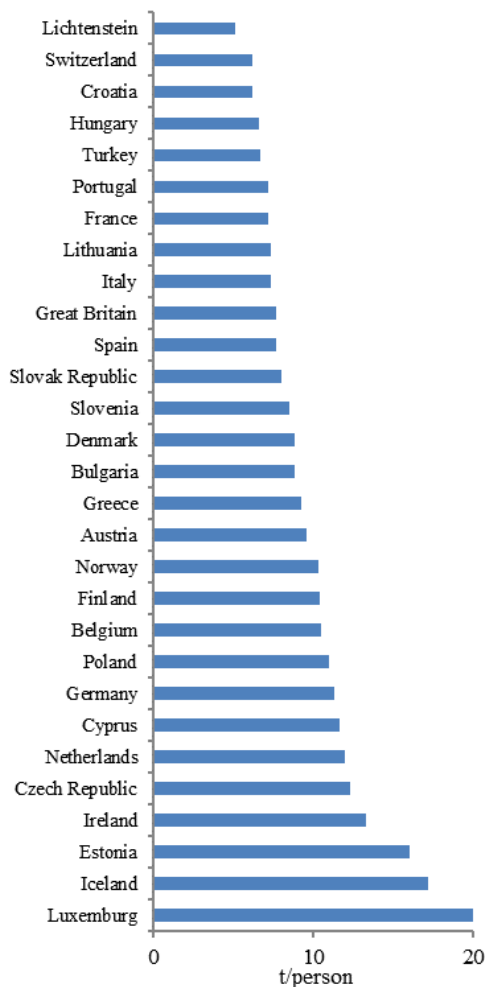


Figure 2. Greenhouse gas emissions in tonnes per capita for 2017, according to the European Environment Agency [5]

The lead smelting slag and matte from Pb batteries contain Pb in metallic form, as well as in the form of galena (PbS). Iron is present in the stone as FeS (troilite) and FeO (wüstite). The slag contains Fe₂SiO₄ phases as well as FeS. In addition to these phases, impurities, such as Ca and Si are present in the rock and slag. The authors of the study [6] focused on the selective leaching of Pb from stone and slag.

The goal of the study in this paper is to describe the thermodynamic conditions of the

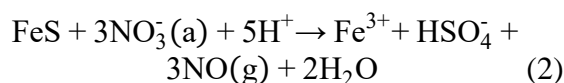
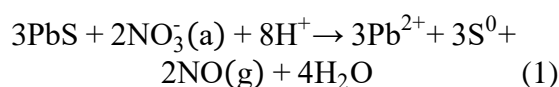
process of leaching of individual phases of stone and slag containing Pb by calculating standard Gibbs energies of reactions (ΔG°_T), enthalpy change (ΔH°_T), entropy of reaction (ΔS°_T) and the equilibrium constant K [mol⁻¹ dm³] at different temperatures in the range of 25 °C to 200 °C. Another objective is to propose a possible way to eliminate emissions emerging during the process.

EXPERIMENTAL

The chemical reaction equations (1) – (4) describe the leaching of Pb and Fe from galena (PbS) and troilite (FeS) in nitric acid. For the given chemical reactions, the values of the change of standard Gibbs energies (ΔG°_T), as well as other thermodynamic quantities at temperatures from 25 °C to 200 °C, were calculated using the HSC Chemistry program (HSC version 6.1) [8], which are summarized in the Tables 1 - 5.

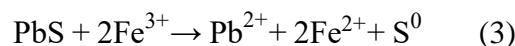
RESULTS AND DISCUSSION

Equations (1) and (2) describe the leaching of lead and iron (from PbS, FeS) in nitric acid, with the formation of NO (g).



Thermodynamic quantities for equations (1) and (2) are shown in Tables 1 and 2.

During the leaching of FeS, Fe³⁺ is formed, which acts as an oxidizing agent, thus allowing further leaching of Pb from galena to form Fe²⁺ ions (equation (3)).



Thermodynamic quantities for equation (3) are shown in Table 3.

Table 1. Thermodynamic quantities for equation (1) calculated using the HSC Chemistry program (HSC version 6.1)

T, K	ΔH°_T , kJ	ΔS°_T , J K ⁻¹	ΔG°_T , kJ mol ⁻¹	K, mol ⁻¹ dm ³	Log(K)
298.15	-125.718	142.758	-168.281	3.053E + 029	29.485
318.15	-123.119	151.193	-171.222	1.300E + 028	28.114
338.15	-120.498	159.185	-174.326	8.526E + 026	26.931
358.15	-117.896	166.659	-177.585	7.985E + 025	25.902
378.15	-114.729	175.264	-181.005	1.011E + 025	25.005
398.15	-109.540	188.628	-184.642	1.682E + 024	24.226
418.15	-106.886	195.133	-188.480	3.521E + 023	23.547
438.15	-104.159	201.500	-192.446	8.803E + 022	22.945
458.15	-101.509	207.415	-196.537	2.567E + 022	22.409
473.15	-125.718	142.758	-168.281	3.053E + 029	29.485

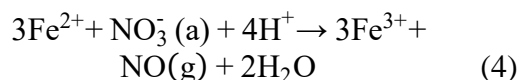
Table 2. Thermodynamic quantities for equation (2) calculated using the HSC Chemistry program (HSC version 6.1)

T, K	ΔH°_T , kJ	ΔS°_T , J K ⁻¹	ΔG°_T , kJ mol ⁻¹	K, mol ⁻¹ dm ³	Log(K)
298.15	-515.136	125.289	-552.491	6.342E + 096	96.802
318.15	-508.917	145.492	-555.205	1.454E + 091	91.163
338.15	-503.383	162.372	-558.289	1.766E + 086	86.247
358.15	-498.344	176.853	-561.684	8.436E + 081	81.926
378.15	-493.718	189.427	-565.350	1.258E + 078	78.100
398.15	-489.477	200.361	-569.250	4.877E + 074	74.688
418.15	-487.105	206.200	-573.328	4.219E + 071	71.625
438.15	-482.992	215.811	-577.549	7.230E + 068	68.859
458.15	-479.064	224.579	-581.955	2.267E + 066	66.355
473.15	-476.255	230.613	-585.369	4.254E + 064	64.629

Table 3. Thermodynamic quantities for equation (3) calculated using the HSC Chemistry program (HSC version 6.1)

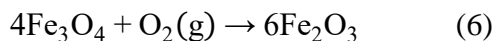
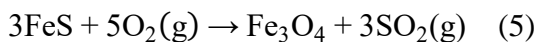
T, K	ΔH°_T , kJ	ΔS°_T , J K ⁻¹	ΔG°_T , kJ mol ⁻¹	K, mol ⁻¹ dm ³	Log(K)
298.15	13.867	302.458	-76.311	2.347E + 013	13.370
318.15	14.150	303.375	-82.368	3.346E + 013	13.525
338.15	14.616	304.793	-88.449	4.614E + 013	13.664
358.15	15.269	306.664	-94.563	6.205E + 013	13.793
378.15	16.547	310.133	-100.730	8.226E + 013	13.915
398.15	19.490	317.707	-107.005	1.095E + 014	14.040
418.15	21.152	321.777	-113.399	1.468E + 014	14.167
438.15	23.383	326.981	-119.883	1.965E + 014	14.293
458.15	26.208	333.281	-126.485	2.642E + 014	14.422
473.15	28.694	338.617	-131.523	3.320E + 014	14.521

From the obtained values of ΔG°_T it is evident that the probability of reactions (1) - (3) increases with increasing temperature. In nitric acid, ferrous ions are oxidized to ferric ions to form NO(g) (equation (4)).



Thermodynamic quantities for equation (4) are shown in Table 4.

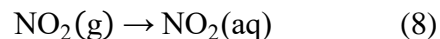
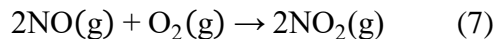
In order to prevent leaching of Fe into the solution, oxidative roasting in the temperature range 400 - 700 °C is beneficial (equations (5) and (6)):



The troilite (FeS) in the matte (or other wastes containing Pb, Zn, Cu) is then transformed into a more stable form as magnetite (Fe₃O₄). Of course, this causes SO₂ and vapours of As₂O₃ to get released during the roasting.

Currently, there is a trend to abandon roasting processes that produce emissions and replace them by leaching in an autoclave at temperatures above 120 °C and higher pressures. Suitable alternative is the pressure oxidation leaching at temperatures in the range

150 - 220 °C. NO(g) released in the pressure vessel during leaching of the waste is oxidizing to NO₂(g) and subsequently regenerating autocatalytically to NO₂(aq) (equations (7) and (8)).



Equation (9) describes the oxidation of elemental sulphur formed during the leaching of sulphides in the HNO₃ medium (equation (1)) to H₂SO₄ during the process.



Thermodynamic quantities for equation (9) are shown in Table 5.

Table 4. Thermodynamic quantities for equation (4) calculated using the HSC chemistry program (HSC version 6.1)

T, K	ΔH° _T , kJ	ΔS° _T , J K ⁻¹	ΔG° _T , kJ mol ⁻¹	K, mol ⁻¹ dm ³	Log(K)
298.15	-147.091	-312.866	-55.375	7.374E + 009	9.868
318.15	-145.955	-309.055	-52.265	1.015E + 009	9.006
338.15	-144.867	-305.522	-49.193	1.608E + 008	8.206
358.15	-143.840	-302.293	-46.154	2.891E + 007	7.461
378.15	-142.879	-299.363	-43.146	5.826E + 006	6.765
398.15	-141.986	-296.722	-40.166	1.302E + 006	6.115
418.15	-141.173	-294.388	-37.210	3.193E + 005	5.504
438.15	-140.449	-292.364	-34.277	8.525E + 004	4.931
458.15	-139.822	-290.661	-31.362	2.458E + 004	4.390

Table 5. Thermodynamic quantities for equation (9) calculated using the HSC chemistry program (HSC version 6.1)

T, K	ΔH° _T , kJ	ΔS° _T , J K ⁻¹	ΔG° _T , kJ mol ⁻¹	K, mol ⁻¹ dm ³	Log(K)
298.15	-315.379	114.364	-349.477	1.706E + 061	61.232
318.15	-317.163	108.571	-351.705	5.605E + 057	57.749
338.15	-318.845	103.443	-353.824	4.575E + 054	54.660
358.15	-320.536	98.585	-355.844	7.993E + 051	51.903
378.15	-322.725	92.640	-357.757	2.641E + 049	49.422
398.15	-326.467	83.004	-359.515	1.479E + 047	47.170
418.15	-328.820	77.242	-361.119	1.301E + 045	45.114
438.15	-331.624	70.697	-362.600	1.704E + 043	43.232
458.15	-334.888	63.416	-363.942	3.143E + 041	41.497

The meaning of the other calculated constants can be summarized as the following. If the equilibrium constant K is < 1 (or $\log(K) < 0$) the reaction goes to the left. If the equilibrium constant K is > 1 (or $\log(K) > 0$) the reaction goes to the right. The value of K for all calculated reaction equations is over one, ensuring that reactions take place in the direction of products. Negative enthalpy of reaction ΔH°_T for chemical reactions (1), (2), (4) and (9) means that the reactions are exothermic, positive enthalpy ΔH°_T of the reaction (3) means that the reaction is endothermic. Entropy changes of the reaction ΔS°_T (chemical reaction (4)) were negative, and that means that the process was spontaneous and did not require any other chemicals.

Among other things, the autoclave decomposes $\text{Fe}(\text{NO}_3)_3$ to form hematite and $\text{NO}(\text{g})$ and a small proportion of $\text{NO}_2(\text{g})$. In a closed system, nitrogen oxide is regenerating to nitric acid. The advantage of a closed system compared to atmospheric leaching is that the regeneration of HNO_3 in the autoclave (higher temperatures) allows the use of a lower concentration of acid, and at the same time allows to achieve a higher oxidation-reduction potential. Hydrometallurgical processes allow to reduce or eliminate emissions that would occur in pyrometallurgy or conventional leaching processes without using an autoclave.

CONCLUSION

Efforts to reduce greenhouse gas emissions and meet the commitments under the Kyoto Protocol (to the 2005 UN Framework Convention on Climate Change) and the 2015 Paris Climate Agreement are forcing EU countries to look for solutions to reduce their carbon footprint and become carbon neutral. Reduction of SO_2 and NO_x emissions in the EU within the last three decades was significant. Between 1990 and 2015, SO_x emissions in the EU and NO_x emissions decreased by 89 %. The energy sector remains a problem, in which new ones have not replaced old technologies due to financial

demands, and therefore the production of emissions in 2020 is still not close to zero. SO_2 and NO_x emissions are also produced in the metallurgical industry. The most common sources are pyrometallurgical operations of roasting and melting of sulphidic and sulphur-containing raw materials (e.g., reducing agents). However, a potential source of these emissions can also be the hydrometallurgical recovery of Pb from intermediates obtained by melting Pb accumulators, i.e., from Pb matte and slag. The thermodynamic calculations performed in this work for the individual reactions that can take place in the leaching of galena or magnetite with nitric acid show that the production of gaseous NO_x is spontaneous. Therefore, it is necessary to look for effective modifications of technologies or new methods of processing Pb matte or slag. One possibility is to replace atmospheric leaching of Pb matte in HNO_3 , which produces gaseous NO_x , by autoclave leaching. With this change, it is possible to achieve the desired selective leaching of lead from iron, to prevent the production of NO_x emissions and also to reduce the consumption of leaching agent (HNO_3). The technology provides the possibility to omit the oxidative roasting step, which is undesirable for high energy demands and the production of $\text{SO}_2(\text{g})$.

REFERENCES

- [1] J. Ye, J. Shang, Q. Li, W. Xu, J. Liu, X. Feng, T. Zhu, The use of vacuum ultraviolet irradiation to oxidize SO_2 and NO_x for simultaneous desulfurization and denitrification, *Journal of Hazardous Material* 271(2014), 89-97.
- [2] The European Pollutant Release and Transfer Register, <https://prtr.eea.europa.eu/#/home>, Accessed: April 20, 2020.
- [3] <https://airindex.eea.europa.eu/>, Accessed: April 20, 2020.
- [4] The Copernicus Atmosphere Monitoring Service (CAMS), <https://www.copernicus.eu/en/services/atmosphere>, Accessed: February 10, 2020.

- [5] Greenhouse gas emissions per capita, <https://ec.europa.eu/eurostat>, Accessed: February 10, 2020.
- [6] A. Akcil, H. Ciftci, Metals recovery from multimetal sulphide concentrates (CuFeS₂-PbS-ZnS): combination of thermal process and pressure leaching, International Journal of Mineral Processing 71(2003) 1-4, 233-246.
- [7] L. Zhang, Z. Xu, A review of current progress of recycling technologies for metals from waste electrical and electronic equipment, Journal of Cleaner Production 127(2016), 19-36.
- [8] HSC Chemistry, 2007. Chemical Reaction and Equilibrium Software with Extensive Thermochemical Database. ver. 6.1., Outotec Research Oy Piori, Finland.

Acknowledgements

This work was supported by the Slovak Research and Development Agency under contract No. APVV-14-0591.