

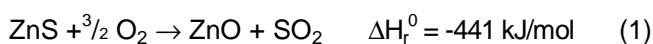
SOLAR THERMAL EXTRACTION OF COPPER AND ZINC FROM SULFIDES

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A novel approach for extracting metals from metal sulfides is proposed. Key feature is the use of concentrated solar radiation to directly convert metal sulfides into the metal and sulfur. Such processes have the potential to produce metals with virtually zero emission of SO_2 and CO_2 . The feasibility of such a solar thermal extraction has been evaluated for zinc sulfide (ZnS) and copper(I)sulfide Cu_2S . Thermodynamic calculations suggest that for both processes heat recovery from the hot product is required to implement a viable process. Decomposition experiments have indicated that the high reactivity of Zn and S is not compatible with the energy requirement of heat recovery and that quenching will likely be needed to collect Zn. As an alternative, the addition of a mixture of O_2 and steam (chemical quenching) is discussed. The extraction of Cu from Cu_2S appears less critical: Experiments under N_2 revealed the formation of metallic Cu already at 1323 K. Natural separation of gaseous S from liquid Cu successfully prevents recombination of the two products and at least partial heat recovery can be envisaged.

1 INTRODUCTION

Most of the commercially important non-ferrous metals such as copper, zinc, nickel or lead are mined as sulfides. Carbothermic processes as they were implemented e.g. for the extraction of iron from iron oxide can not be applied, since carbon-sulfur compounds are not stable enough to drive the reaction of metal sulfide with carbon. Therefore, conventional extraction processes include roasting to convert the metal sulfide into the corresponding metal oxide, and as a second step the extraction of the metal from the metal oxide. This production scheme implicates two serious disadvantages [1]: Firstly, roasting of the sulfides liberates corrosive and toxic sulfur dioxide (SO_2). Reaction 1 describes the roasting of zinc sulfide (ZnS). Although SO_2 is nowadays often used for on-site production of sulfuric acid, emission of SO_2 still causes severe damages to the local environment. Secondly, metal extraction from the relatively stable intermediate metal oxide by either a pyrometallurgical or an electrolytic process produces vast amounts of CO_2 . In the former process carbonaceous materials are added as combustible and as reducing agent, in the latter, electricity generation is the source for CO_2 emission.



The decreasing demand for sulfuric acid and attempts to reduce CO_2 emissions stimulated research activities aiming at direct conversion of sulfides to the metal and elementary sulfur. Direct conversion provides two benefits: i) SO_2 emission will be avoided and elementary sulfur can be stored for later usage or deposition and ii) the total energy demand for the metal extraction will be lower, since the energy-intensive reduction of the intermediate metal oxide is avoided. Reaction 2 exemplifies the decomposition of ZnS into Zn and S. Even though research resulted in valuable process adaptations, direct conversion of sulfides into metal and sulfur is still an unresolved problem.

A promising approach to realize direct conversion is the use of concentrated solar radiation. Thermodynamic analyses indicated that many sulfides decompose to the metal and sulfur under inert atmospheres at temperatures between 1500 and 2500 K. Such temperatures are readily accessible in solar

furnaces. To explore the feasibility of direct reduction of metal sulfides under concentrated solar radiation, a study on the decomposition of synthetic ZnS and Cu_2S was initiated.

2 DECOMPOSITION OF ZINC SULFIDE

The energetics of the decomposition of ZnS is illustrated by means of the enthalpy-entropy- (Mollier-) diagram. Mollier diagrams contain the enthalpy as variable. Thus, enthalpy differences can be immediately read from the diagram. For reversible processes the slope of the curves represent the equilibrium temperature. Figure 1 shows that the decomposition of solid ZnS into gaseous zinc Zn(g) and sulfur $\text{S}_2(\text{g})$ is endothermic by 396 kJ/mol. The equilibrium temperature was calculated to be 1824 K. From Figure 1 one can appreciate that the moderate equilibrium temperature is mainly due to the high reaction entropy which results from the formation of gaseous products. Formation of gaseous products on the other hand accounts for 50% of the reaction enthalpy. This figure suggests that heat recovery from the hot products is strongly desirable for implementing a viable production of solar Zn from ZnS .

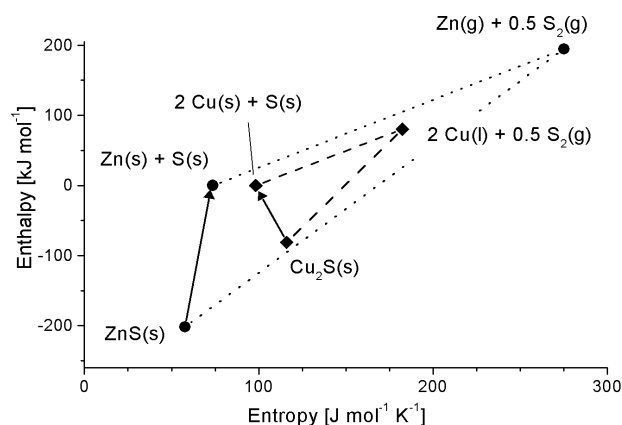
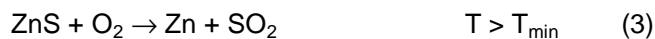


Fig. 1: Enthalpy-Entropy diagram for the decomposition of ZnS (dotted line) and Cu_2S (dashed line).

Experimental studies on the decomposition of ZnS were initiated with experiments in a tube furnace interfaced to a quench unit under nominally inert atmosphere ($p(\text{O}_2) \leq 8 \cdot 10^{-2}$ mbar). At temperatures up to 1800 K no metallic Zn but ZnS was found on the cool

finger of the quench unit. These results indicate that recombination of Zn and S is probably as difficult to suppress as the oxidation of Zn vapour in the presence of O₂ and that rigorous measures will be needed to prevent recombination.

While physical quenching represents the only means to avoid oxidation of Zn by O₂, alternative routes can be envisioned for the system Zn–S:



Thermodynamic calculations show that Zn besides SO₂ is formed at temperatures above a minimum working temperature T_{\min} and with stoichiometric amounts of O₂ (see reaction 3). Below T_{\min} reaction 4 proceeds to the right and undesired ZnO besides S is formed. However, we expect that the reaction of Zn with the relatively stable SO₂ is slow enough such that Zn can be cooled to room temperature and collected with good yields even at moderate cooling rates. Recombination of Zn with S can also be suppressed by the addition of steam. We expect an endothermic reaction, with SO₂ and H₂ being the products. By using concentrated solar radiation as heat source this reaction combines the extraction of zinc with the solar production of hydrogen. Thermodynamic calculations show that the addition of steam as quenching agent decreases the minimum working temperature and the amount of the side-product ZnO. The reaction however suffers from low yields. Only 5 mol-% of the added water react with ZnS to form Zn, SO₂ and H₂.

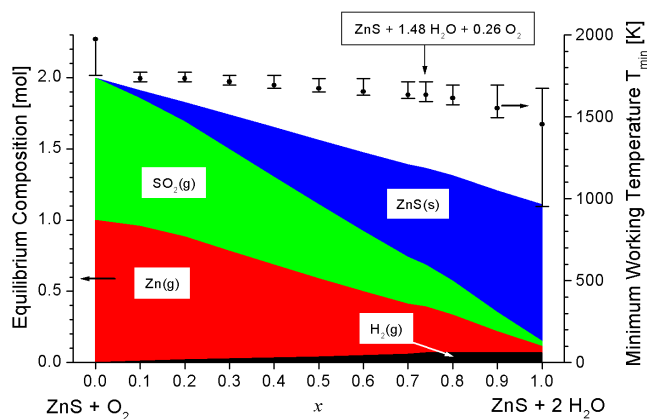


Fig. 2: Calculated equilibrium composition for the system $\text{ZnS} + 2x \text{H}_2\text{O} + (1-x) \text{O}_2$ at the minimum working temperature T_{\min} at atmospheric pressure. Compounds with concentrations less than 0.03 mol (S, H₂S) and ZnS were omitted for clarity.

An interesting feature was observed when ZnS was reacted with mixtures of O₂ and steam. At a composition of 0.26 O₂ and 1.48 H₂O the reaction enthalpy is close to zero.

In summary, chemical quenching allows for direct extraction of Zn from ZnS. Although the approach does not reduce the SO₂ emission, it offers a path for an autothermal process for direct extraction of Zn from ZnS with zero CO₂ emission.

3 DECOMPOSITION OF COPPER SULFIDE

The situation looks different for copper sulfide (Cu₂S). The direct solarthermal decomposition of Cu₂S is promising from the viewpoint of avoiding both SO₂ and CO₂. Because Cu is more noble than Zn, less energy is needed for decomposing Cu₂S into molten copper Cu(l) and gaseous sulfur S₂(g) than for decomposing ZnS. Although there is no evaporation of Cu, heat stored in the hot products accounts for 50% of the total reaction enthalpy and heat recovery appears desirable. Unlike recombination of Zn and S, recombination of Cu and S is not expected to be a major obstacle since separation of Cu melt and S vapour will occur naturally in the course of the reaction. Experiments under an inert gas flow ($p(\text{O}_2) \leq 8 \cdot 10^{-2}$ mbar) produced Cu at temperatures as low as 1323 K.

4 SUMMARY AND CONCLUSION

Direct reduction of metal sulfides produces the metal and elementary sulfur. When concentrated solar radiation is used to effect the reduction, processes with virtually no emission of SO₂ and CO₂ can be envisioned. Therefore, a benefit for the local environment and the global climate is expected.

Preliminary studies on the decomposition of ZnS indicated that strong measures, e.g. fast cooling, will be needed to prevent the products Zn and S from reacting after they will have left a solar reactor. To estimate the cooling rates, data on the chemical kinetics are needed. These studies are scheduled as soon as the experiment for studying the oxidation of Zn by O₂ will be available (see Ref. [2]). An alternative approach to prevent recombination is the addition of an O₂/steam mixture. Such a process can not reduce the SO₂ emission but allows an autothermal extraction of Zn with no CO₂ emissions.

Decomposition of Cu₂S appears easier to realize. Metallic Cu was obtained already at 1323 K and natural separation of the products Cu and S should facilitate heat recovery. Solar thermal extraction of Cu is therefore attractive from both the viewpoint of reducing SO₂ and CO₂ emissions.

This report focussed on ZnS and Cu₂S. However, the above made considerations are not limited to these compounds and further investigations will include any metal sulfide of technical relevance.

5 ACKNOWLEDGEMENT

We would like to thank A. Frei and Th. Frey for experimental support. Continuous financial support from the Swiss Federal Office of Energy is gratefully acknowledged.

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