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Thermodynamic interferences of HCl and HF in producer gas desulfurization by Ce, La, Mn and Zn based solid sorbents

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1. Introduction

Producer gas from gasification processes of coals, biomass and waste fuels can be used for generation of electricity, production of hydrogen, synthetic transportation fuels and chemicals. The advanced applications of syngas (e.g. catalytic processes and fueling of high temperature fuel cells) require deep removal of contaminants (HCl, HF, H₂S, COS organic sulfur compounds, tar compounds, volatile heavy metal compounds etc.) usually present in syngas. Their concentrations in syngas to be cleaned depends on fuel and conditions of gasification (moving/fixed bed, fluidized bed, entrained flow etc.). Among the gas contaminants, sulfur compounds, HCl and HF produced in the gasification process (e.g. fluidized bed process) belong to the most dangerous, which must be removed. Deep producer gas cleaning for attaining sulfur compounds and hydrogen-halides concentrations approx. below 1 ppm_v (or even below 10 ppb_v) requires either application of low temperature wet absorption processes or, particularly for fueling of high temperature fuel cells (SOFC), deployment of medium and high temperature (approx. 500 – 1200 K) cleaning methods based on reactions of gas impurities with solid sorbents. The important factors for hot syngas desulfurization and de-halogenation by solid sorbents are: attainable equilibrium concentrations at given gas composition and operating conditions (temperature, pressure), stability of the sorbents (sintering, melting, evaporation etc.), possible regeneration of a spent sorbent and price.

In literature mainly sorbents based on CaO, ZnO, Fe, Cu and Mn oxides are mentioned for removal of sulfur compounds (H₂S, COS) [1-4]. Recently also sorbents based on rare earth oxides have been studied (both theoretically and experimentally) for deep syngas desulfurization [5-9]. Possibilities of removal of HCl from syngas by transition metals [1,9,10] and alkali based sorbents [1,11,12] at temperatures 200 – 800 °C have shown on possible applicability of soda and K₂CO₃ based sorbents. Interferences of HCl and HF in H₂S sorption by solid sorbents at higher temperatures have been studied only rarely [1,13]. Particularly studies (both, theoretical and experimental) of interferences in sulfur compounds sorption caused by HF and interferences of H₂S in HF removal by alkali sorbents are missing in available literature.

The theoretical thermodynamic study of desulfurization and simultaneous interferences caused by presence of HCl and HF is complicated in the case of rare earth oxides (Ce_2O_3 , CeO_2 , La_2O_3 , Nd_2O_3 , etc.) by lack of reliable thermodynamic data (particularly ΔG_f°) for solid products of desulfurization (oxy-sulfides), particularly for temperatures between 400 and 800 K [14,15]. Also the data for $\text{Ce}_2\text{O}_2\text{S}$ and $\text{La}_2\text{O}_2\text{S}$ at 298.15 K are scarce and partly disputable [15,16].

In our thermodynamic theoretical study we concentrated our attention on thermodynamics of gas-solid desulfurization reactions (H_2S , COS, thiophene), properties of sorbents (melting point evaporation), attainable equilibrium sulfur compounds concentrations in gas at temperature 500 – 1100 K (227-827 °C) under conditions typical for producer gas composition. Similarly removal of HCl and HF by Ce, La, Zn, Mn and Ni oxides based sorbents is described and possible interferences in simultaneous sorption of HCl or HF with H_2S are analyzed. Suitable conditions and sorbents are suggested for deep removal of sulfur compounds in presence of HCl. Conditions for efficient preliminary removal of HCl and HF by alkali-based sorbents (NaHCO_3 , K_2CO_3 , $\text{Ca}(\text{OH})_2$, CaCO_3) are suggested and possible interferences caused by H_2S are analyzed in terms of attainable equilibrium concentrations of HCl and HF in presence of H_2S . Properties of La and Ce-based sorbents for sulfur compounds are compared with Zn, Mn and Ni based sorbents in terms of efficiency and interferences caused by presence of hydrogen-halides (HCl, HF).

2. Chemistry and Thermodynamics of Desulfurization and Removal of HCl (HF)

For theoretical studies of syngas desulfurization and interferences caused by HCl and HF in sulfur compounds sorption under reducing conditions we have chosen the main input oxides: Ce_2O_3 , CeO_2 , La_2O_3 , ZnO, MnO, Cu_2O and NiO. The considered products of desulfurization reactions under reducing conditions are cerium oxy-sulfide ($\text{Ce}_2\text{O}_2\text{S}$), lanthanum oxy-sulfide ($\text{La}_2\text{O}_2\text{S}$), zinc sulfide (ZnS), manganese sulfide (MnS), cuprous sulfide (Cu_2S) and nickel sulfide (NiS) respectively. The two considered cerium oxides (Ce_2O_3 and CeO_2) are in fact limits in composition of Ce-oxide in real producer gas. As it was proved, the stoichiometry in cerium oxides varies approx. between $\text{CeO}_{1.6}$ and $\text{CeO}_{1.85}$ according to intensity of reduction conditions and temperature [6,8,17]. At temperatures over 800 K and under strongly reducing conditions the final composition of cerium oxide is close to Ce_2O_3 . Formation of Ce_2S_3 and La_2S_3 is possible only under extreme conditions (high pressures of H_2S , S_n , H_2 , CO and very low pressures of H_2O vapor and CO_2). Under “usual” reduction conditions prevailing in syngas only the mentioned La and Ce oxy-sulfides are stable. Some transition and uncertainty in stoichiometry exists even in the case of $\text{Ce}_2\text{O}_2\text{S}$. It is interesting to note that existence of $\text{Ce}_2\text{O}_{2.5}\text{S}$ has been clearly proved and properties of it were described [18].

Reactions of the above mentioned oxides with HCl lead to corresponding chlorides: CeCl_3 , LaCl_3 , ZnCl_2 , MnCl_2 , CuCl and NiCl_2 . In the case of lanthanum, also oxy-chloride is stable and can be considered as one of the products (LaOCl , LaCl_3) of the reaction of La_2O_3 with HCl. On the other hand, CeOCl is extremely unstable and is not considered here as possible product. In the case of reactions of HF with the mentioned oxides, generally only corresponding fluorides are formed. The values of Gibbs energy of formation (ΔG_f°) of the compounds have been taken mostly from Barin tables [19]. The data for thiophene have been overtaken from J. Phys. Chem. Ref. Data [20]. The ΔG_f° data for $\text{Ce}_2\text{O}_2\text{S}$ and $\text{La}_2\text{O}_2\text{S}$ have been overtaken from other sources [6,14-16] and partly either interpolated or determined under assumption of linear dependence on temperature.

For reactions with HF and interferences in H₂S sorption, fluorides ZnF₂, MnF₂, NiF₂ and CuF have been considered as products. The products of hydrogen fluoride (HF) reaction with La₂O₃ and Ce₂O₃ can be both, corresponding fluorides (LaF₃, CeF₃) or oxy-fluorides (LaOF, CeOF). The mentioned oxy-fluorides exist, have interesting physical (electric and optic) properties and both are relatively stable, but literature data on ΔG_f and ΔG_r for their reactions are available in literature [21] only for LaOF.

Removal of HCl and HF from syngas by gas-solid reactions [1,11,22] with Na₂CO₃, K₂CO₃, and calcium based sorbents (Ca-hydroxide and carbonate) have been considered.

The Gibbs energies ΔG_r for individual reactions have been computed according to reaction stoichiometry and the general scheme:

$$\Delta G_r = \Sigma(\Delta G_f)_{\text{final compounds}} - \Sigma(\Delta G_f)_{\text{input compounds}} \quad (1.1)$$

The equilibrium reaction constant K_{eq} is thermodynamically related with ΔG_r, absolute temperature T and the universal gas constant R through the following equation:

$$\ln(K_r) = [-\Delta G_r/(RT)] \quad \text{or} \quad K_r = \exp[-\Delta G_r/(RT)] \quad (1.2)$$

Computation of equilibrium pressures of gas or volatile species from the equilibrium constant is described elsewhere [23,24]. For simplicity unit activities of all solid reactants (compounds and elements) were considered in computations of equilibrium gas phase composition (partial pressures).

ZnCl₂, MnCl₂, CuCl and partially CaCl₂ are the main easy melting compounds (< 800 °C) among the reaction products (**Table I**). Moreover elemental Zn is relatively volatile.

Table I: Melting points (lower than 800 °C) and boiling points of selected compounds and metallic Zn relevant in removal reactions of H₂S, HCl and HF from producer gas

Compounds	Melting point (°C)	Boiling point (°C)	Notice
ZnCl ₂	292 (565 K)	756	Relatively volatile
Zn	419 (692.7 K)	907	Relatively volatile
CuCl	426 (771 K)	1490	
MnCl ₂	650 (923 K)	1225	
KCl	770 (1043 K)	1420	
CaCl ₂	772 (1045 K)		
NiS	797 (1070 K)	1388	

3. Results and discussion

Desulfurization of syngas (Removal of H₂S, COS and thiophene)

The equilibrium concentrations of H₂S and COS in reactions with ZnO, MnO, Cu₂O, Ce₂O₃, CeO₂ and La₂O₃ at atmospheric pressure (1 bar) under assumption of 40 vol. % of hydrogen, 10 vol. % of water vapor and 30 vol. % of CO₂ in gas phase are shown in **Figs 1 and 2**. As it is obvious (**Fig. 1**), CeO₂ is not suitable for syngas desulfurization and must be reduced to Ce₂O₃

prior to reaction with H₂S. At temperatures 600 – 800 K the ZnO, Cu₂O, Ce₂O₃ and La₂O₃ based sorbents are able to ensure output concentrations of H₂S and COS below 1 ppm_v ($P_{\text{H}_2\text{S}} < 10^{-6}$ bar) and below 10⁻² ppm_v ($P_{\text{COS}} < 10^{-8}$ bar) respectively. Cu₂O exerts the lowest attainable H₂S and COS equilibrium pressures (concentrations) in the frame of the sorbents studied ($P_{\text{H}_2\text{S}} < 10^{-9}$ bar).

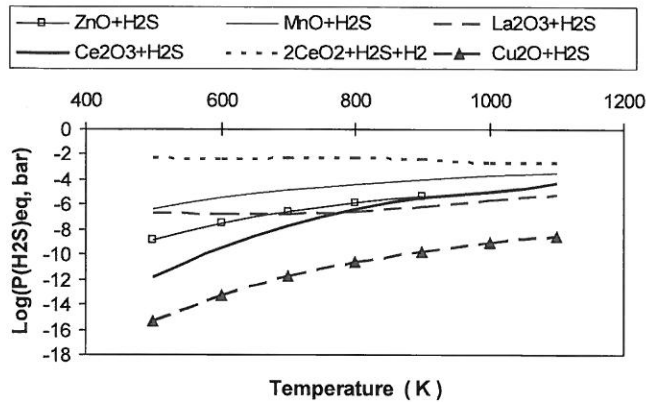


Fig. 1: Dependence of equilibrium H₂S pressures (expressed as log($P_{\text{H}_2\text{S}}$ - in bar)) on temperature in reactions of H₂S with the selected solid sorbents ($P_{\text{H}_2} = 0.4$ bar, $p_{\text{H}_2\text{O}} = 0.1$ bar)

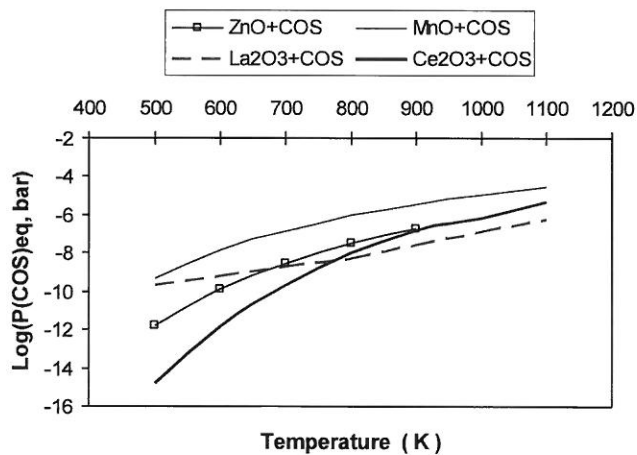


Fig. 2: Dependence of equilibrium COS pressures (expressed in log(P_{COS} - in bar)) on temperature in reactions of COS with the selected solid sorbents ($P_{\text{CO}_2} = 0.3$ bar)

Attaining of equilibrium concentrations of H₂S below 1 ppb_v is theoretically possible only with Cu₂O at temperatures below 1000 K or with Ce₂O₃ based sorbents at lower temperature (< 600 K). The theoretically attainable equilibrium COS pressures are generally lower than the H₂S equilibrium pressures. Very low equilibriums H₂S pressures (corresponding concentrations below 1 ppb_v) are exerted by the reaction of elemental Zn with H₂S (**Table II**). The lowest equilibrium

H₂S pressures are thus enabled by Cu₂O or metallic zinc as solid input reagents. Stability of Zn and Cu₂O under “usual conditions” prevailing in producer gas is, however, practically excluded. ZnO is reducible to metallic Zn only at extreme reducing conditions (gas composition with very low H₂O and CO₂ content). Copper(I) oxide (Cu₂O) in on the other hand easily reducible to metallic Cu at very low P_{H₂}/P_{H₂O} ratio in syngas). Stability of Cu₂O is improved in mixtures with TiO₂ or with some other stable metal oxides. NiO is reducible to Ni at higher temperatures under typical syngas composition. Reduction of Ce₂O₃ and La₂O₃ by syngas to metallic form of Ce and La is thermodynamically excluded.

Table II: Comparison of equilibrium concentrations of H₂S for reactions of Zn, ZnO, Ni, NiO, Cu and Cu₂O with H₂S at supposed partial pressure of H₂O vapors 0.1 bar and hydrogen pressure = 0.4 bar. The stable forms (in common raw producer gas) are marked in bold.

Reaction	H ₂ S-equil. conc. at 500 K (bar)	H ₂ S-equil. conc. at 700 K (bar)	H ₂ S-equil. conc. at 900 K (bar)
Zn + H ₂ S = ZnS + H ₂	2.00 E-17	4.91 E-12	5.86 E-09
ZnO + H₂S = ZnS + H₂O	1.53 E-09	2.74 E-07	4.91 E-06
Ni + H₂S = NiS + H₂	1.53 E-05	1.08 E-03	8,56 E-03
NiO + H ₂ S = NiS + H ₂ O	6.88 E-09	8.23 E-07	9.72 E-06
2Cu + H₂S = Cu₂S + H₂	1.90 E-06	4.93 E-05	2.42 E-04
Cu ₂ O + H ₂ S = Cu ₂ S + H ₂ O	4.22 E-16	1.85 E-12	1.75 E-10

Producer gas from fluidized bed or fixed bed gasification of solid fuels with sulfur content can contain various organic sulfur compounds. According to general experience the most abundant organic sulfur compound in such a gas is thiophene. In the case of thiophene desulfurization reactions, the possible reaction outputs include water vapor, carbon (soot), benzene, CH₄, alkenes, acetylene and other products. The majority of thiophene desulfurization reactions have very high equilibrium constant (resulting very low equilibrium P_{thiophene}) – exceptions are mainly the reactions leading to formation of alkenes/alkanes. For two temperatures (800 and 1000 K), selected/assumed partial pressures of gas components (P_{H₂} = 0.4 bar, P_{H₂O} = 0.1 bar, P_{CO} = P_{CO₂} = 0.2 bar and P_{CH₄} = P_{Benzene} = P_{Acetylene} = P_{C₂H₄} = P_{butene} = 0.01 bar) and two sorbents (Ce₂O₃ and NiO) the equilibrium thiophene pressures are shown in **Table III**. The reactions with alkenes (ethylene and 1-butene) as products/reaction outputs are marked in bold.

The mechanism of thiophene reactions with metal oxides or metals (e.g. Ni) is relatively complicated involving physical sorption and formation of bonds with sulfur. The syngas components play a significant role and it is clear, that presence of higher concentration of benzene, alkenes and methane in gas causes higher concentrations of thiophene in gas. This is typical situation in co-gasification of coal or wood with plastics (PET, polypropylene etc.) It seems that the experimental experience is confirmed and explained also by thermodynamics.

Table III: Selected reactions of thiophene (C₄H₄S) with Ce₂O₃ and NiO – equilibrium partial pressures of thiophene at 800 K and at 1000 K (P_{CO} = P_{CO₂} = 0.2 bar, P_{H₂} = 0.4 bar, P_{H₂O} = 0.1 bar, P_{minorite} = 0.01 bar)

Reaction	P _{thiophene} at 800 K (bar)	P _{thiophene} at 1000 K (bar)
Ce ₂ O ₃ + C ₄ H ₄ S + C ₂ H ₂ + H ₂ = benzene + H ₂ O(g) + Ce ₂ O ₂ S	2.66 E-17	3.15 E-12
NiO + C ₄ H ₄ S + C ₂ H ₂ + H ₂ = benzene + H ₂ O(g) + NiS	2.02 E-16	7.37 E-12
Ce ₂ O ₃ + C ₄ H ₄ S + 3H ₂ = 2CH ₄ + H ₂ O(g) + 2C + Ce ₂ O ₂ S	2.81 E-23	5.00 E-18
NiO + C ₄ H ₄ S + 3H ₂ = 2CH ₄ + H ₂ O(g) + 2C + NiS	2.14 E-22	1.17 E-17
Ce₂O₃ + C₄H₄S + 2H₂ + CO = 1-butene + CO₂ + Ce₂O₂S	1.55 E-07	8.51 E-04
NiO + C₄H₄S + 2H₂ + CO = 1-butene + CO₂ + NiS	1.18 E-06	1.99 E-03
Ce ₂ O ₃ + C ₄ H ₄ S + ethylene = benzene + H ₂ O(g) + Ce ₂ O ₂ S	1.78 E-12	7.95 E-10
NiO + C ₄ H ₄ S + ethylene = benzene + H ₂ O(g) + NiS	1.35 E-11	1.86 E-09
Ce ₂ O ₃ + C ₄ H ₄ S = C ₂ H ₂ + H ₂ O(g) + 2C + Ce ₂ O ₂ S	2.73 E-10	2.88 E-10
NiO + C ₄ H ₄ S = C ₂ H ₂ + H ₂ O(g) + 2C + NiS	2.09 E-09	6.73 E-10
Ce₂O₃ + C₄H₄S + CO + 2H₂ = CO₂ + 2C₂H₄ + Ce₂O₂S	1.22 E-09	3.07 E-07
NiO + C₄H₄S + CO + 2H₂ = CO₂ + 2C₂H₄ + NiS	9.32 E-09	7.17 E-07

For application of mixed sorbents for H₂S/COS removal interactions of the oxide sorbents with other sulfides (competitive sorption) are important. The interaction of Ce₂O₃ with ZnS, MnS, NiS and mutual interaction of NiS, MnS and Cu₂S with ZnO are thermodynamically assessed in **Table IV**. The interactions are usually more significant at lower temperatures (e.g. 600 K). Stability of MnS in presence of ZnO and Ce₂O₃ is weak. Stability of Cu₂S in mixture with ZnO depends extremely on presence of hydrogen and water vapor in gas (ratio of P_{H₂}/P_{H₂O}). Ce₂O₃ can pull the sulfur out from MnS, NiS and even ZnS. In reality those solid-solid reactions run with sufficient speed only at temperatures over the Taman temperature when the crystal lattice is more pliant/movable.

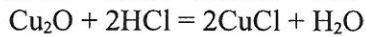
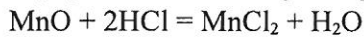
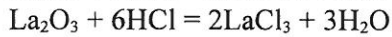
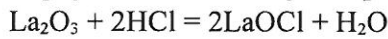
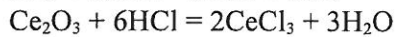
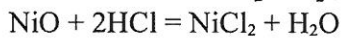
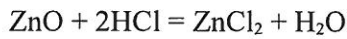
Table IV: Thermodynamic equilibria in solid-solid reactions among Ce₂O₃ and other sulfides, ZnO and other sulfides and one reaction involving also hydrogen at 600 K and 1000 K

Reaction	Δ G _r (kJ/mol)		K _{eq} (-)	
	600 K	1000 K	600 K	1000 K
ZnS + Ce ₂ O ₃ = ZnO + Ce ₂ O ₂ S	-22.495	-2.665	90.87	1.37
MnS + Ce ₂ O ₃ = MnO + Ce ₂ O ₂ S	-45.527	-24.063	9196.5	18.07
NiS + Ce ₂ O ₃ = NiO + Ce ₂ O ₂ S	-29.039	-7.068	337.41	2.33
NiS + ZnO = NiO + ZnS	-6.544	-4.403	3.71	1.69
MnS + ZnO = ZnS + MnO	-23.032	-21.398	101.2	13.11
Cu ₂ S + ZnO = ZnS + Cu ₂ O	65.894	80.353	1.83 E-06	6.35 E-05
Cu ₂ S + ZnO + H ₂ = ZnS + 2Cu + H ₂ O(g)	-23.252	-16.853	105.76	7.59

Dehalogenation of syngas (removal of HCl and HF) by desulfurization sorbents

If the producer gas (syngas) contains HCl and HF, generally the sulfur sorbents can react with them. In the case of reactions of hydrogen chloride the following reactions have been assumed:

The products of the reactions of HCl with the metal oxides sorbents (primarily intended for sulfur removal) are generally corresponding chlorides. Only in the case of La_2O_3 two products have been taken into consideration: lanthanum oxy-chloride (LaOCl) and lanthanum(III) chloride (LaCl_3):



The computed equilibrium HCl pressures are shown in **Fig. 3**, where they are compared with equilibrium HCl pressure in reaction of classic HCl sorbent (soda):

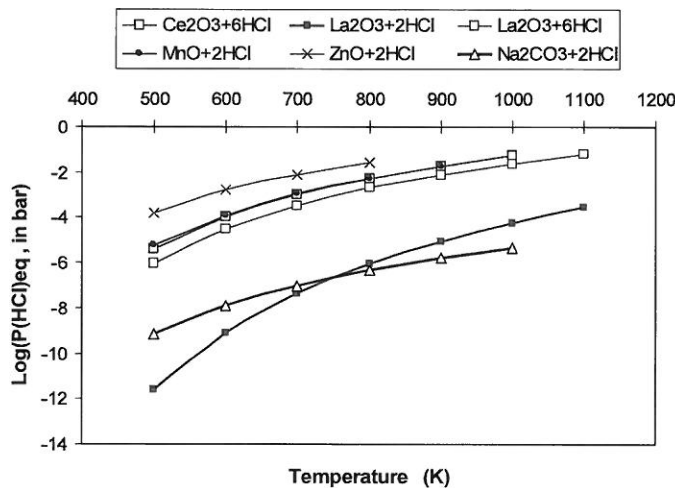
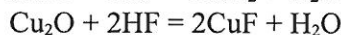
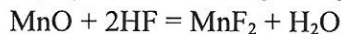
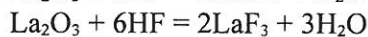
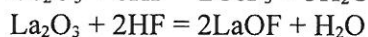
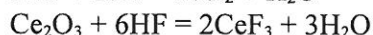
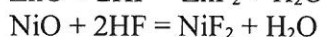
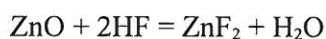


Fig. 3: Dependence of equilibrium HCl pressures on temperature for ZnO, MnO, NiO, La_2O_3 and Ce_2O_3 solid sorbents (assumed $P_{\text{H}_2\text{O}} = 0.1$ bar, $P_{\text{CO}_2} = 0.2$ bar)

The values of equilibrium pressures of HCl in the case of Cu_2O reaction are in a region between the reactions of La_2O_3 with HCl and for NiO the $(P_{\text{HCl}})_{\text{eq}}$ are slightly above the equilibrium

pressures of HCl for ZnO sorbent. As it follows from the Fig. 3 practically only the La_2O_3 sorbent (under conditions of LaOCl formation) can remove efficiently HCl at temperatures below approx. 800 K. The Cu_2O sorbents can remove efficiently HCl (it means equil. $P_{\text{HCl}} < 10^{-6}$ bar) only at temperatures approx. below 600 K. ZnO, NiO, MnO and Ce_2O_3 sorbents have weaker equilibrium sorption of HCl (inapplicable for realistic conditions of syngas cleaning).

For removal of hydrogen fluoride (HF) from syngas the following reactions have been thermodynamically analyzed:



Similarly as for the reactions of La_2O_3 with HCl two products of reaction with HF have been assumed: lanthanum oxy-fluoride (LaOF) and lanthanum(III) fluoride (LaF_3).

The computed equilibrium HF pressures are shown in Fig. 4, where they are compared with equilibrium HF pressure in reaction of classic HCl sorbent (soda):

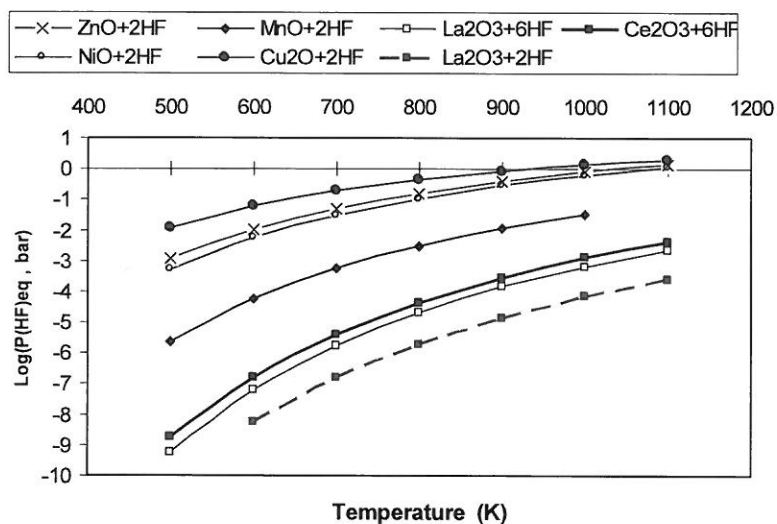


Fig. 4: Dependence of equilibrium HF pressures on temperature for ZnO, MnO, NiO, Cu_2O , La_2O_3 and Ce_2O_3 solid sorbents (assumed $P_{\text{H}_2\text{O}} = 0.1$ bar, $P_{\text{CO}_2} = 0.2$ bar)

As it is obvious (Fig. 4) only the La_2O_3 and Ce_2O_3 based sorbents have ability to remove efficiently HF from gases (equil. $P_{\text{HF}} < 10^{-6}$ bar) at temperatures below approx. 700-750 K. The ZnO , Cu_2O and NiO based sorbents are inefficient in HF sorption.

Interferences caused by HCl and HF in gas desulfurization (H_2S sorption)

For the HCl caused interference in gas desulfurization the following reactions were taken into consideration in thermodynamic analyses:

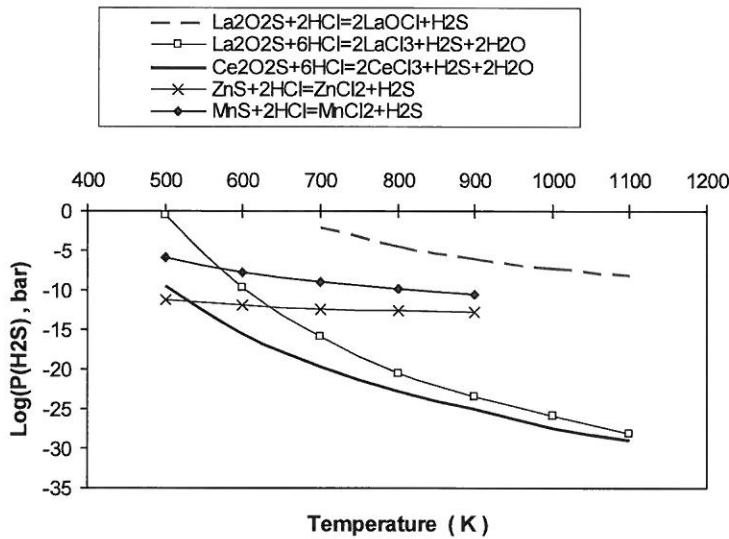
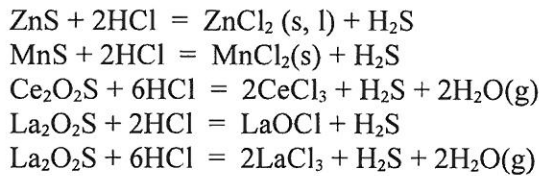


Fig. 5: Dependence of equilibrium H_2S pressures (expressed as $\log(P_{\text{H}_2\text{S}} - \text{in bar})$) on temperature in reactions of selected sulfides with HCl ($P_{\text{H}_2\text{O}} = 0.1$ bar, $P_{\text{HCl}} = 10^{-5}$ bar)

The equilibrium H_2S pressures for reaction of Cu_2S with HCl are between $(P_{\text{H}_2\text{S}})_{\text{eq}}$ for reactions of ZnS and MnS with HCl. The equil. $P_{\text{H}_2\text{S}}$ pressures in reaction of NiS with HCl are similar to $(P_{\text{H}_2\text{S}})_{\text{eq}}$ in reaction of ZnS with HCl. The strongest interference of HCl in desulfurization is found for La_2O_3 , but only for reaction with HCl leading to LaOCl formation. Therefore the $\text{La}_2\text{O}_3/\text{La}_2\text{O}_2\text{S}$ based sorbents of H_2S could be ineffective in gases with concentrations of HCl above approx. 5 ppm_v. On the other hand the ZnO/ZnS and $\text{Ce}_2\text{O}_3/\text{Ce}_2\text{O}_2\text{S}$ based sorbents are resistant to interferences of HCl in gas desulfurization (H_2S sorption). However, for the cerium oxide/oxy-sulfide based sorbents, very strong dependence of interferences on HCl concentration (proportional to $(P_{\text{HCl}})^6$) has to be taken into account – as it is shown in Fig. 6

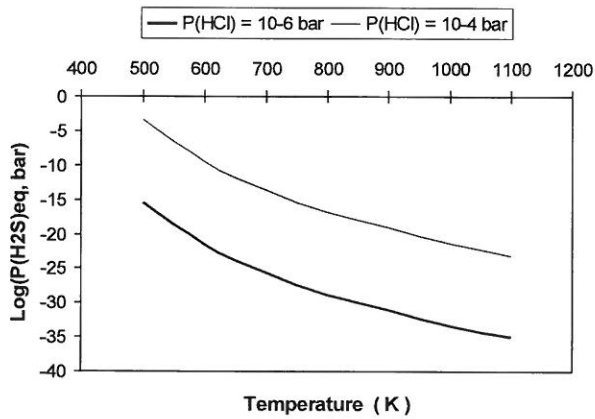


Fig. 6 : Effect of P_{HCl} on dependence of equilibrium H_2S pressures on temperature for the reaction $\text{Ce}_2\text{O}_2\text{S} + 6 \text{HCl} = 2\text{CeCl}_3 + 2\text{H}_2\text{O} + \text{H}_2\text{S}$ (assumed $P_{\text{H}_2\text{O}} = 0.1 \text{ bar}$).

Interferences in gas desulfurization caused by presence of HF in syngas have been analyzed for the following reactions:

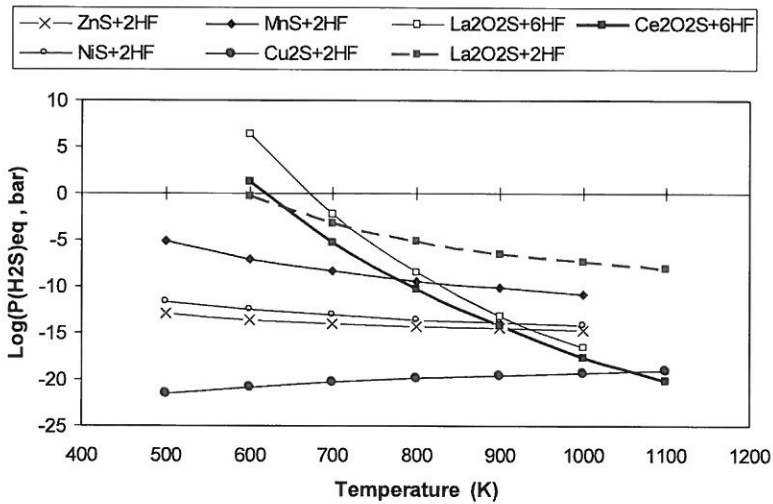
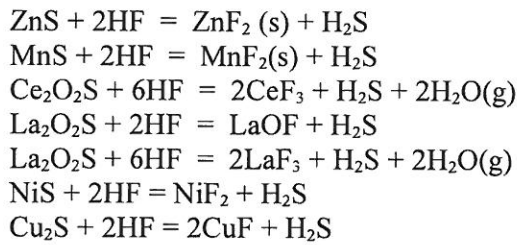


Fig. 7 : Dependence of equilibrium H_2S pressures (expressed as $\log(P_{H_2S}$ - in bar)) on temperature in reactions of sulfides with HF ($P_{H_2O} = 0.1$ bar, $P_{HF} = 10^{-5}$ bar)

Presence of low HF concentration in syngas has very significant effect on efficiency of H_2S sorption mainly for La_2O_3/La_2O_2S and Ce_2O_3/Ce_2O_2S sorbents, partially on MnO/MnS sulfur sorbents. The cerium based sorbents are suitable for desulfurization in gases with some HF content rather at temperatures over 800 K. The Cu, Zn and Ni based sorbents do not suffer from interferences from the side of HF in gas desulfurization.

Removal of HCl and HF by Na_2CO_3 , K_2CO_3 and calcium based sorbents

Na_2CO_3 , K_2CO_3 and partly calcium based sorbents are suitable for removal of HCl from gases at temperatures approx. 500- 900 K. Higher temperatures are unsuitable for soda and K_2CO_3 based sorbents because at temperatures over approx. 900 K formation of eutectics with melting points below 1000 K should be expected. At water vapor and CO_2 concentrations between 5 and 20 vol. % the attainable equilibrium concentrations of HCl are below 1 ppm_v [22]. K_2CO_3 is a more efficient sorbent than the soda based sorbents. With K_2CO_3 (theoretically) HCl concentrations in gas lower than approx. 10 ppb_v are attainable.

Situation in HF equilibrium sorption is different from HCl sorption by the alkali sorbents (**Fig. 8**): the Na_2CO_3 and K_2CO_3 sorbents are generally worse than calcium compounds based sorbents (e.g. $Ca(OH)_2$ and $CaCO_3$). With Na_2CO_3 sorbents the HF concentrations lower than 1 ppm_v are theoretically attainable only at temperatures below 600 K and at low H_2O and CO_2 concentrations. K_2CO_3 is even excluded for such gas cleaning (de-HF) requirements. The Ca-based sorbents (both calcium hydroxide and calcium carbonate) show better results in HF equilibrium removal from gas phase in a temperature range 500 – 900 K (**Fig. 8**).

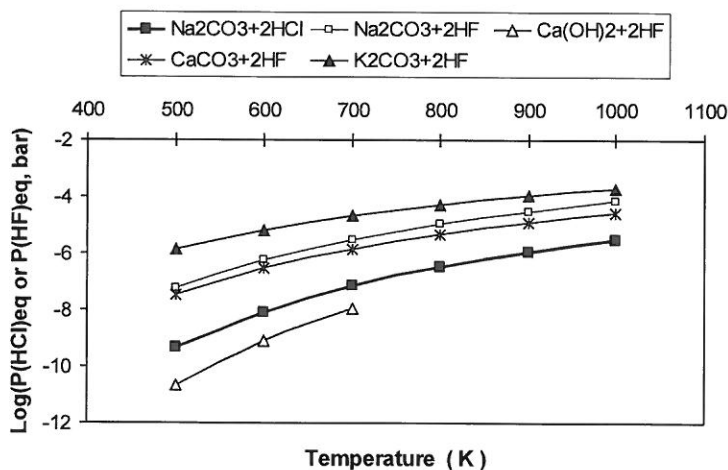
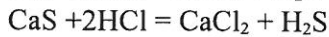
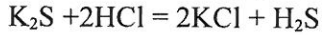
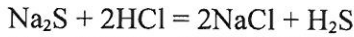


Fig. 8: Dependence of equilibrium HF or HCl concentrations (expressed as $\log(P_{HF}$ - in bar) or $\log(P_{HCl}$ - in bar)) on temperature for Na_2CO_3 , K_2CO_3 , $Ca(OH)_2$ and $CaCO_3$ based sorbents ($P_{H_2O} = P_{CO_2} = 0.1$ bar)

Interferences caused by H₂S presence in HCl and HF removal by alkali-sorbents

For the thermodynamic study of H₂S interferences in HCl sorption reaction the following reactions have been assumed:



The results of computations of equilibrium HCl pressures under assumption of $P_{\text{H}_2\text{S}} = 0,001$ bar are shown in **Fig. 9**. As clearly visible, the HCl sorption by Na₂CO₃ and K₂CO₃ sorbents enables at presence of 1000 ppm_v of H₂S still attaining of equilibrium HCl concentrations in gas below approx. 1 ppb_v at temperature below 700 K.

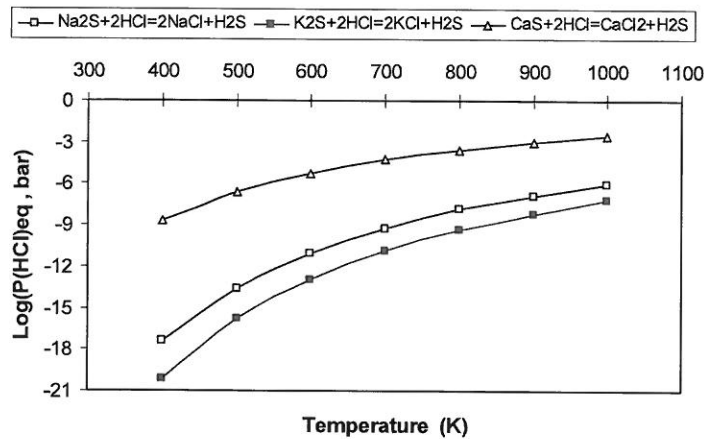
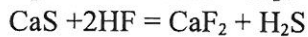
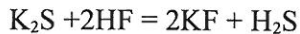
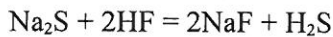


Fig. 9: Interference of H₂S in sorption of HCl by alkali sorbents expresses as dependence of equilibrium HCl pressures in indicated reaction systems with $P_{\text{H}_2\text{S}} = 10^{-3}$ bar

Another situation is in HF sorption in presence of higher concentrations (partial pressures) of H₂S. For a similar system of reactions as in the case of HCl sorption:



The results of computations of equilibrium HF pressures at $P_{\text{H}_2\text{S}} = 0.001$ bar are shown in **Fig. 10**. The equilibrium concentrations of HF lower than approx. 1 ppb_v can be attained only at low temperatures (approx. for $T < 600$ K) and rather with Na₂CO₃/Na₂S based sorbents. On the other hand the calcium hydroxide based sorbents are less sensitive on H₂S presence in HF removal than in HCl sorption.

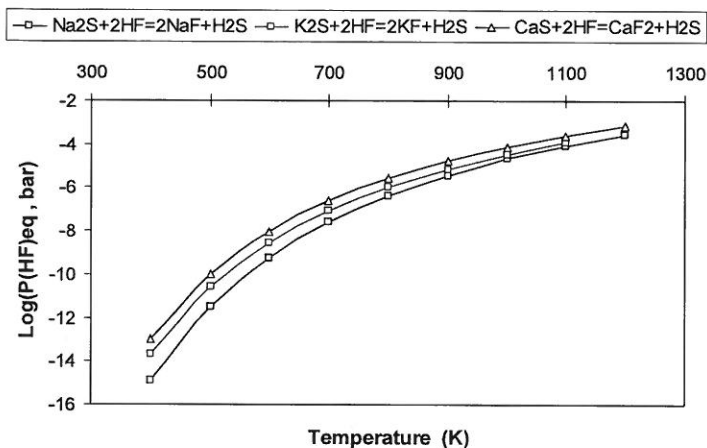


Fig. 10: Interference of H₂S in sorption of HF by alkali sorbents expresses as dependence of equilibrium HF pressures in indicated reaction systems with $P_{\text{H}_2\text{S}} = 10^{-3}$ bar

4. Conclusions

Ce₂O₃ and La₂O₃ based sorbents of sulfur compounds (H₂S COS, thiophene) are at least comparable with ZnO based sorbents at temperatures between 600 and 800 K. MnO is the less suitable H₂S sorbent. CeO₂ is not suitable sorbent of sulfur compounds at all and must be used only in a pre-reduced state (Ce_xO_y). Ce₂O₃ enables theoretically (similarly as Cu₂O) achievement of H₂S equilibrium concentrations lower than 1 ppb-v in gas at temperatures below 600 K. Copper(I) oxide (Cu₂O) could be a very efficient H₂S sorbent, but due to easy reduction of Cu₂O in syngas to less efficient elemental Cu, its applicability is thermodynamically weaker in comparison with ZnO or Ce₂O₃. Deepness of removal of thiophene and similar organic sulfur compounds depends on presence of mainly higher alkenes/alkanes (propene/propane, butane/butane, ethylene, etc.) in gas. With their higher concentrations, it seems, the equilibrium thiophene concentrations increase. The other removal/destruction reactions of thiophene (e.g. by means of Ce₂O₃ or NiO) indicate thermodynamic viability of its very deep removal from syngas.

Applicability of mixed (binary, ternary) sorbents of sulfur compounds is influenced by interactions of the formed sulfides with metal oxides present. The interactions are usually more significant at lower temperatures (e.g. 600 K). Stability of MnS in presence of ZnO and Ce₂O₃ is weak. Stability of Cu₂S in mixture with ZnO depends extremely on presence of hydrogen and water vapor in gas (ratio of $P_{\text{H}_2}/P_{\text{H}_2\text{O}}$). Cerium oxide (Ce₂O₃) can pull the sulfur out from MnS, NiS and even from ZnS. In reality, however, those solid-solid reactions run with sufficient speed only at higher temperatures (over the Tamam temperature).

Reactions of HCl and HF with sulfur sorbents can be significant mainly at lower temperatures. Practically only the La₂O₃ sorbent (under conditions of LaOCl formation) can remove efficiently HCl at temperatures below approx. 800 K. The Cu₂O sorbents can remove efficiently HCl (it means equilibrium $P_{\text{HCl}} < 10^{-6}$ bar) only at temperatures approx. below 600 K. ZnO, NiO, MnO and Ce₂O₃ sorbents have weaker equilibrium sorption of HCl (inapplicable for realistic conditions of syngas cleaning). In HF removal by the studied sorbents, similarly as for the

reactions of La_2O_3 with HCl, two products of reaction with HF are realistically possible: lanthanum oxy-fluoride (LaOF) and lanthanum(III) fluoride (LaF_3). Only the La_2O_3 and Ce_2O_3 sorbents have ability to remove efficiently HF from gases (equilibrium $P_{\text{HF}} < 10^{-6}$ bar) at temperatures below approx. 750 K. The ZnO, Cu_2O and NiO based sorbents are inefficient in HF sorption from syngas.

Interferences of HCl and HF in H_2S removal reactions are not important in the case of ZnO. Conditions preferring formation of LaOCl or LaOF (higher H_2O concentrations in gas, lower temperatures) exclude the La-based sorbents of H_2S , because of significant interference in sorption from the side of HCl and HF.

The strongest interference of HCl in desulfurization (removal of H_2S from gas) was found for La_2O_3 , but only for reaction with HCl leading to LaOCl formation. Therefore the $\text{La}_2\text{O}_3/\text{La}_2\text{O}_2\text{S}$ based sorbents of H_2S could be ineffective for desulfurization in gases with concentrations of HCl above approx. 5 ppm_v. On the other hand, the ZnO/ZnS and $\text{Ce}_2\text{O}_3/\text{Ce}_2\text{O}_2\text{S}$ based sorbents are resistant to interferences of HCl in gas desulfurization (H_2S sorption). However, for the cerium oxide/oxy-sulfide based sorbents, very strong dependence of interferences on HCl concentration (proportional to $(P_{\text{HCl}})^6$) has to be taken into account. At temperatures over 600 K Ce_2O_3 based sorbents exert the lowest attainable equilibrium concentration of H_2S , however presence of HCl in gas has tremendous effect on attainable equilibrium concentrations of H_2S . Interference of HF is even worse than the HCl effects in gas desulfurization. The Ce_2O_3 and La_2O_3 sorbents are not applicable in such a case at temperatures below 800 K. On the other hand interferences of HF in ZnS formation and H_2S sorption are weaker than the effects of HCl.

Presence of low HF concentration in syngas has very significant effects on efficiency of H_2S sorption mainly for $\text{La}_2\text{O}_3/\text{La}_2\text{O}_2\text{S}$ and $\text{Ce}_2\text{O}_3/\text{Ce}_2\text{O}_2\text{S}$ sorbents, partially on MnO/MnS sulfur sorbents. The cerium based sorbents are suitable for desulfurization in gases with some HF content rather at higher temperatures over 800 K. The Cu, Zn and Ni based sorbents do not suffer from interferences from the side of HF in gas desulfurization.

Hydrogen chloride can be removed at temperatures between approx. 500 and 900 K by soda and K_2CO_3 based sorbents. With K_2CO_3 it is possible to attain equilibrium concentrations of HCl in gas on a level of 10 ppb_v. The equilibrium sorption of HF by alkaline sorbents presents a more complicated matter. The common alkali carbonates (Na_2CO_3 and K_2CO_3) are surprisingly less suitable for removal of HF than the calcium based sorbents ($\text{Ca}(\text{OH})_2$ and CaCO_3). The otherwise reactive K_2CO_3 sorbent is unable to remove HF from syngas on a level around 1 ppm_v. Attaining of HF concentration in gas below approx. 10 ppb_v is possible only by means of $\text{Ca}(\text{OH})_2$ or CaO based sorbents at temperatures below 650 – 700 K. The interferences of H_2S in dehalogenation (de-HCl and de-HF) of syngas by soda and K_2CO_3 based sorbents are generally more important in HF removal.

Acknowledgements

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References

- [1] J. Lee, B. Feng, A thermodynamic study of the removal of HCl and H₂S from syngas, *Front. Chem. Sci. Eng.* 6(1), (2012) 67-83.
- [2] X. Meng, W. de Jong, R. Pal, A.H.M. Verkooijen, In bed and downstream hot gas desulphurization during solid fuel gasification: A review, *Fuel Processing Technology* 91, (2010) 964-981.
- [3] W.F. Elseviers, H. Verelst, Transition metal oxides for hot gas desulphurization, *Fuel* 78, (1999) 601-612.
- [4] S. Cheah, D.L. Carpenter, K.A. Magrini-Bair, Review of Mid- to High-Temperature Sulfur Sorbents for Desulfurization of Biomass- and Coal-derived Syngas, *Energy and Fuels* 23, (2009) 5291-5307.
- [5] M. Flytzani-Stephanopoulos, M. Sakbodin, Z. Wang, Regenerative Adsorption and Removal of H₂S from Hot Fuel Gas Streams by Rare Earth Oxides, *Science*, 312, (2006) 1508-1510.
- [6] D.A.R. Kay, W.G. Wilson, V. Jalan, High temperature thermodynamics and applications of rare compounds containing oxygen and sulphur in fuel gas desulphurization and SO_x and NO_x removal, *Journal of Alloys and Compounds*, 192, (1993) 11-16.
- [7] I. Valsamakis, R. Si, M. Flytzani-Stephanopoulos, Stability of lanthanum oxide-based H₂S sorbents in realistic fuel processor/fuel cell operation, *Journal of Power Sources*, 195, (2010) 2815-2822.
- [8] Y. Zeng, S. Kaytakoglu, D.P. Harrison, Reduced cerium oxide as an efficient and durable high temperature desulfurization sorbent, *Chem. Eng. Sci.*, 55, (2000) 4893-4900.
- [9] P.J. Woolcock, R.C. Brown, A review of cleaning technologies for biomass-derived syngas, *Biomass and Bioenergy*, 52, (2013) 54-84.
- [10] T.K. Tseng, L. Wang, H. Chu, High temperature cleaning for chlorine-containing coal gas by supported Manganese oxide sorbent, *Aerosol and Air Quality Research*, 12, (2012) 961-971..
- [11] J. Kapfenberg, J. Sohnemann, D. Schleitzer, A. Loewen, Acid gas removal by customized sorbents for integrated gasification fuel cell systems, 5-th Internat. Symposium on Gas cleaning at high temperatures, Morgantown, Wv, USA, September 17-20, 2002..
- [12] R.A. Newby, T.E. Lippert, R.B. Slimane, O.M. Akpolat, K. Pandya, F.S. Lau, J. Abbasian, B.E. Williams D. Leppin, Novel gas cleaning/conditioning for integrated gasification combined cycle, Base program final report, prepared for DOE by Siemens Westinghouse Power corporation and Gas technology institute (DOE Aw. No.: DE-AC26-99FT40674), USA, August 2001.
- [13] R.P. Gupta, W.S. O'Brien, Desulfurization of hot flue syngas containing hydrogen chloride vapours using zinc titanate sorbents, *Ind. Eng. Chem. Res.*, 39, (2000) 610-619.
- [14] R. Akila, K.T. Jacob, A.K. Shukla, Gibbs energies of formation of rare earth oxy-sulfides, *Metallurgical Transactions B*, 18B, (1987) 163-168.
- [15] Ju.L. Suponitzky, V.L. Laptev, Thermodynamics of the formation of oxo-sulfides of rare-earth elements, *Russian Chemical Bulletin*, 46, No. 2, (1997) 279-283.
- [16] V.R. Kalakota, Sulfur removal using regenerable sorbents of rare earth/Transition metal oxides, Ph.D. Thesis, Dep. of Chem. Eng., Louisiana State University, USA, 2008.

- [17] A. Trovarelli, Catalytic Properties of Ceria and CeO₂-Containing Materials, *Catalysis Reviews: Science and Engineering*, 38(4), (2006) 439-520.
- [18] W. Suski, T. Palewski T.: Ce₂O_{2.5}S in Ternary pnictides and chalcogenides containing s-, p- or f-electron elements, *Landolt Börnstein – Group III Condensed Matter, Numerical data and Functional Relationships in Science and technology*, vol. 27B5, Pnictides and Chalcogenides II, Edited by H. P. J Wijn, p. 1072-1073 (2003).
- [19] I. Barin, O. Knacke, *Thermochemical data of pure substances*. 3rd ed. Weinheim: VCH; 1995.
- [20] O.V. Dorofeeva, L.V. Gurvich, Ideal gas thermodynamic properties of sulfur heterocyclic compounds, *J. Phys Chem. Ref. Data* (1995) 1351-1376.
- [21] K.T. Jacob, V.S. Saji, Lanthanum Oxyfluorides: Structure, Stability and Ionic Conductivity, *Int. J. Appl. Ceram. Technol.* 3(4), (2006) 312-321.
- [22] K. Svoboda, M. Hartman, M. Pohořelý, M. Šyc, P. Kameníková, M. Jeremiáš, L.-W. Huang, Thermodynamic possibilities and limits for producer gas desulfurization and HCl related interferences for Zn, Mn, Ce and La based sorbents of sulfur compounds, lecture presented on IC3MT 2014 Internat. Conf., Taipei, Taiwan, September 1-5, 2014.
- [23] K. Svoboda, G. Slowinski, J. Rogut, D. Baxter, Thermodynamic possibilities and constraints for pure hydrogen production by iron based chemical looping process at lower temperatures, *Energy Conversion and Manag.* 48 (2007) 3063–3073.
- [24] K. Svoboda, M. Hartman, Y.-P. Chyou, P. Kameníková, M. Pohořelý, M. Šyc, Thermodynamic possibilities of producer gas desulfurization and dechlorination by Ce, La, and Mn based solid sorbents and regeneration of sorbents after sulfidation, presentation on the Internat. Conf. of SSCHE, Tatranské Matliare, Slovakia, May 25-28 (2014).