Kinetic Features of the Hydrogen Sulfide Sorption on the Ferro-Manganese Material

Elizaveta Cheremisina 1, Olga Cheremisina 2, Maria Ponomareva 2, Viktor Bolotov 2 and Alexander Fedorov 2,*

1 K1-MET GmbH, Stahlstraße 14, A-4020 Linz, Austria; Elizaveta.Cheremisina@k1-met.com
2 Department of Physical Chemistry, Faculty of Mineral Processing, Saint Petersburg Mining University, 199106 St. Petersburg, Russia; Cheremisina_OV@pers.spmi.ru (O.C.); Ponomareva_MA@pers.spmi.ru (M.P.); s185095@stud.spmi.ru (V.B.)
* Correspondence: fedorov_at@pers.spmi.ru; Tel.: +7-9-046-322-412

Abstract: The kinetics of hydrogen sulfide sorption by the surface of a ferromanganese material containing in its composition a mixture of iron (II) and (III) oxides FeO × Fe₂O₃, takakelitē (Mn, Ca) Mn₃O₄ × 3H₂O and quartz SiO₂, and which is samples of unrefined ferromanganese ore, was studied in this work. Sorption rate constant and activation energy constant values were calculated. The catalytic effect of iron (III) oxide was established, the presence of which in natural material contributes to a decrease in the H₂S sorption activation energy. Based on the results of X-ray phase and chromatographic analysis methods, a chemical (redox) reaction of the conversion of hydrogen sulfide into elemental sulfur and H₂O was revealed. The overall process rate is expressed in terms of the physical sorption stage and chemical transformation of the components; the influence of the rate of the third stage—reaction products desorption—on the overall rate of the process is taken into account. The limiting stage of the process is determined—a chemical reaction. The relation between the heat and the activation energy of the chemical transformation is used according to the Bronsted—Polanyi rule for catalytic processes. It was found that with an increase in the chemisorption heat, the activation energy of the chemisorption stage decreases and, as a consequence, its rate increases. The sorption process parameters were calculated—the Fe₂O₃ coverage degree with the initial substances and reaction products providing the maximum sorption rate, which can be a criterion for evaluating the catalytically active sites of the catalyst surface for carrying out catalytic reactions.

Keywords: chemisorption; hydrogen sulfide; ferromanganese material; kinetics; activation energy; heterogeneous catalysis

1. Introduction

The emission of waste gases containing toxic substances, including sulfur-containing compounds, is a serious environmental problem of the metallurgical industry [1–6]. Sorption methods are still effective in the field of the air environment cleaning process. Considering the volume of evolved gaseous substances, porous inorganic materials containing substances possessed with oxidative properties to a number of gaseous compounds can be used as promising and inexpensive sorbents [7]. Manganese oxides are widely used in gas cleaning technologies as oxidizing agents. There exist various artificial sorption materials with the manganese oxide film coated surface. Oxidative destruction of phenols and cyanide compounds, sorption of hydrogen sulfide and sulfur (IV) oxide, as well as organic compounds, is taking place on the surface of manganese oxide.

The use of both products and raw materials of metallurgy plants during the gas cleaning process can be cost-effective. Their application will ensure low or even waste-free main production technologies due to the full engagement of the mentioned materials. Reducing the ecological impact on the environment caused by metallurgical enterprises is possible by involving unrefined ferromanganese ores in the technological cycle. Providing high sorption characteristics comparable to the properties of synthesized sorbents based on...
manganese oxide [8], ferromanganese ores can be used in the process of sulfur-containing gas clearing.

The authors of this work investigate the sorption properties of ferromanganese material—unrefined ferromanganese ore samples of the Ulu-Telyaksky deposit (Republic of Bashkortostan), which is the raw material for manganese and iron oxide production. The presence of manganese (IV) and iron (III) compounds in ore samples provides oxidizing properties in relation to gaseous compounds, which contain reducing elements. Iron and manganese oxides can also exhibit catalytic properties. Accordingly, in the process of heterogeneous catalysis, the interaction of the reactant with the surface of the solid catalyst will have a dominant role. Consequently, the nature of physical and chemical interactions with the surface of the ferromanganese material will determine the kinetics of the hydrogen sulfide sorption process, the study of which is the subject of this work.

Since catalysis is a specific phenomenon, only a specific (individual) catalyst can be used for each chemical reaction or process. Zhuravsky et al. investigated the process of hydrogen sulfide sorption on active coals [9], which comes with the oxidation of hydrogen sulfide to elemental sulfur and water due to the presence of nitrogen and oxygen atoms in the coals. Oxidized nitrogen-modified activated carbons were used as a sorbent. As a result of the study, the authors determined the presence of elemental sulfur traces and made a conclusion about the mechanism of electronic catalysis.

Chung Lau L. et al. studied the absorption of $H_2S$ on activated carbon, which was impregnated with a solution of cerium (III) nitrate, washed with sodium hydroxide, filtered, and dried at 80 °C [10]. Kinetic studies were carried out in the temperature range of 30–70 °C. The calculation of kinetic parameters was carried out using pseudo-first and pseudo-second order models according to the equations:

Pseudo-first order
$$n(Q_e - Q_t) = -k_1 + \ln Q_e, \quad (1)$$

Pseudo-second order
$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}, \quad (2)$$

where $Q_t$—adsorption capacity at time $t$; $Q_e$—full sorbent capacity, calculated based on thermodynamic data; $k_1$—pseudo-first order reaction rate constant; $k_2$—pseudo-second order reaction rate constant.

Based on the results of linear dependencies plotting, the authors have chosen a pseudo-second-order calculation model. The calculated values of the reaction rate constants at temperatures of 30, 40, 50, 60, and 70 °C are: \((2.39; 2.73; 3.98; 3.64 \text{ and } 4.07) \times 10^{-6} \text{ g/mg × min},\) the activation energy value was 11.7 kJ/mol.

Aslam Z. et al. investigated the oil fly ash (OFA) collected during the utilization of power plants, which was processed by the method of physicochemical activation to improve the surface properties [11]. The synthesized activated carbon from oil fly ash was used for the adsorption of hydrogen sulfide. The sorbent was obtained by adding a mixture of acids (20% nitric acid and 80% phosphoric acid) to OFA, after which the sorbent was treated with 2 M potassium hydroxide to increase the surface affinity. As a result of the treatment, the sorption capacity of the material in relation to $H_2S$ was increased.

To describe the kinetics of $H_2S$ adsorption on the alkali-modified activated carbon, Thomas, Yoon–Nelson, and Clark models were used, which made it possible to establish the partial dependencies of the flow rate and concentration of $H_2S$ on the adsorption value. The desulfurization kinetics of hot coal gas ($H_2S \text{ 0.25%}, H_2 \text{ 10.6%}, CO \text{ 18%}, \text{ and carrier gas } N_2$) is described by an improved deactivation kinetic model based on the use of the chemical stoichiometric Equation (3) by the authors of [12]:

$$H_2S + 2/3 \text{LaFeO}_3 + 1/3H_2 = 1/3 \text{La}_2\text{O}_2S + 2/3 \text{FeS} + 1/3\text{H}_2\text{O}, \quad (3)$$

The mesoporous zeolite (M41) based sorbent containing LaFeO$_3$ with a molar ratio of elements La/Fe = 1:2 (LF$_2$) and their different percentages (LF$_2$ 40, 50, 60 and 100%) was
used in the mentioned research. According to the percentage, the obtained reaction rate constants were \( k \times 10^3 \ \text{min}^{-1} \times \text{g}^{-1} \) 8.89; 8.52; 7.61 and 2.52. Despite the obvious chemical (redox) interactions between hydrogen sulfide and LaFeO\(_3\), the calculated value of the activation energy did not exceed 25.1 kJ/mol.

Thus, the kinetic dependencies of sorption processes on zeolite and carbonaceous materials impregnated with substances exhibiting oxidizing properties are approximated by the equations of formal kinetics [13]. However, the contribution of physical and chemisorption to the main sorption process, as well as the effect of desorption of reaction products, remains unclear. A quantitative assessment of the catalytic effect of sorption of hydrogen sulfide on the covalent or ionic surfaces of solids has not been given. There is no understanding of the amount of the active surface of the solid phase responsible for the physical sorption effects. This work was carried out in order to determine the kinetic dependencies of the hydrogen sulfide sorption by solid sorbents exhibiting obvious oxidizing properties. Another purpose of this study was to determine the mechanism and to reveal a number of specific features of the heterogeneous process sorption.

2. Materials and Methods

The kinetics of \( \text{H}_2\text{S} \) sorption on ferromanganese ore of the Ulu-Telyaksky deposit was investigated in this work. Samples with a fraction of 1 to 1.6 mm, having a specific surface area of 110 m\(^2\)/g and a pore size of 1.36-10\(^{-8}\) m were selected for the experiment. Sample parameters were determined by thermal nitrogen desorption using a Nova 1000e surface area and pore size analyzer (Quantachrome Instruments, Boynton Beach, FL, USA). The chemical composition of the ore shown in Table 1 is mainly represented by manganese, silicon, aluminium, and iron. Elemental analysis was carried out by X-ray fluorescence using Shimadzu XRF-1800 spectrometer (Shimadzu Corporation, Kyoto, Japan).

| Element | MnO | SiO\(_2\) | Al\(_2\)O\(_3\) | Fe\(_2\)O\(_3\) | CaO | MgO | K\(_2\)O | Na\(_2\)O | SO\(_3\) | Impurities |
|---------|-----|----------|----------------|----------------|-----|-----|--------|--------|-------|------------|
| Content, % | 48.24 | 24.57 | 8.61 | 7.50 | 7.08 | 1.88 | 1.54 | 0.20 | 0.07 | 0.31 |

According to the results of X-ray phase analysis presented in Figure 1 (X-ray diffractometer Shimadzu XRD-7000 manufactured by Shimadzu Corporation, Kyoto, Japan), the natural material contains few crystalline phases, which are a mixture of iron (II) and (III) oxides FeO \(\times\) Fe\(_2\)O\(_3\), takanelite \((\text{Mn,Ca})\text{Mn}_4\text{O}_9 \times 3\text{H}_2\text{O}\) and quartz SiO\(_2\) [14]. The JCPDS-ASTM international X-ray database was used to correlate the peaks with the composition.

![Figure 1](image_url). Results of X-ray phase analysis of the initial ore samples.

Both standard samples of hydrogen sulfide with a \( \text{H}_2\text{S} \) content of 125 ppm and samples of hydrogen sulfide synthesized in a Wurtz flask were used for the experiment. An excess of \( \text{Na}_2\text{S} \) (reagent grade) and phosphoric acid solution at a concentration of 3 mol/L was added to the Wurtz flask. A part of the synthesized hydrogen sulfide was passed...
through a 6 mol/L NaOH solution (Figure 2a), from the other part a 10–20 mL aliquot of H₂S was taken to a gas syringe. An aliquot was transferred in an air-proof glass vessel with a capacity of 260 mL, after preliminary removal of 10–20 mL of air from the vessel, then 1 mL of a gas sample was taken. One gas sample was placed in a 260 mL vessel with 50 ± 2 mg of ore charge, and another gas sample was placed in a vessel of the same volume without ore charge, taking the gas concentration as the initial value. The experimental set-up scheme is shown in Figure 2b.

Figure 2. (a) Hydrogen sulfide synthesis unit: 1—drop funnel, 2—Wurtz flask, 3—sampling fitting with rubber seal, 4—gas syringe, 5—silicone hose, 6—barbotage unit; (b) hydrogen sulfide sorption unit: 1—gas syringe, 2—ore-containing glass vessel for the sorption process, 3—thermostatic jacket.

The studies were carried out at temperatures of 252, 280, 298 K. To reach the equilibrium concentration, the phase contact time was up to 3 h. At certain time intervals from the beginning of the experiment, aliquots of H₂S were sampled with a gas syringe, for hydrogen sulfide content determination by chromatography method using a Thermo Trace GC Ultra gas chromatograph manufactured by Thermo Scientific, Waltham, MA, USA, using the ratio of the peak areas of standard samples (125 ppm H₂S, 134 ppm CH₃SH, and 149 ppm C₂H₅SH in a helium atmosphere). To measure the thermal effect of the sorption process of hydrogen sulfide on ferromanganese material, a calorimetric unit was assembled using an IKA C2000 basic thermochemical gas analyzer (IKA WERKE, 79219 Staufen im Breisgau, Germany).

3. Results and Discussion

As a result of the experiment, the kinetic dependencies of the hydrogen sulfide concentration (C) change on the sorption time were obtained, as shown in Figure 3.

The kinetic parameters were calculated using the laws of formal kinetics. The reaction order was determined by a graphical method of plotting linear forms of kinetic dependencies. The rate constants of the sorption process were calculated using linear forms of the dependence of the H₂S concentration logarithm on the sorption time on ferromanganese ore at temperatures of 252, 280, 298 K, which is presented in Figure 4.

To confirm the first order of the reaction, the periods of half-conversion (sorption) of hydrogen sulfide were determined at various initial concentrations. The obtained kinetic dependencies of the H₂S concentration on time are shown in Figure 5.
3. Results and Discussion

As a result of the experiment, the kinetic dependencies of the hydrogen sulfide concentration ($C$) change on the sorption time were obtained, as shown in Figure 3.

Figure 3. The dependence of the H$_2$S concentration change on the time of sorption on ferroman- ganese material at different temperatures.

The kinetic parameters were calculated using the laws of formal kinetics. The reaction order was determined by a graphical method of plotting linear forms of kinetic dependencies. The rate constants of the sorption process were calculated using linear forms of the dependence of the H$_2$S concentration logarithm on the sorption time on ferromanganese ore at temperatures of 252, 280, 298 K, which is presented in Figure 4.

Figure 4. Linear forms of H$_2$S sorption kinetic dependencies on ferromanganese ore.

Approximation equations, correlation values, and rate constants of the sorption process are presented in Table 2.

Table 2. Results of processing linear forms of kinetic dependencies.

| T, K | Approximation Equation | Correlation Value $R^2$ | Rate Constant $k$ | $\ln k$ |
|------|------------------------|-------------------------|-------------------|---------|
| 252  | $\ln C = -0.0023 \times t - 9.4254$ | 0.98 | $0.0023 \pm 0.0001$ | $-6.03 \pm 0.30$ |
| 280  | $\ln C = -0.0029 \times t - 9.6098$ | 0.99 | $0.0029 \pm 0.0001$ | $-5.84 \pm 0.29$ |
| 298  | $\ln C = -0.0032 \times t - 9.6039$ | 0.97 | $0.0032 \pm 0.0002$ | $-5.74 \pm 0.29$ |
According to the calculations based on Equation (3):

$$ n = 1 + \frac{\ln \left( \frac{t_{1/2}^i}{t_{1/2}^{i+1}} \right)}{\ln \left( \frac{c_{1/2}^i}{c_{1/2}^{i+1}} \right)}, $$

where $t_{1/2}^i$, $t_{1/2}^{i+1}$—half-conversion time at initial concentrations, sec, $C^1 = 1.06 \cdot 10^{-2}$ mol/L, $C^2 = 1.35 \cdot 10^{-2}$ mol/L and $C^3 = 2.89 \cdot 10^{-3}$ mol/L; $c_{1/2}^i$, $c_{1/2}^{i+1}$—half-conversion concentration at initial concentrations $C^1$, $C^2$ and $C^3$, the reaction order within the error tolerance was 1.

Based on the graphical dependence of the reaction rate constant logarithm value on the reciprocal temperature ($\ln k = -470.55 \frac{1}{T} - 4.1644$, $R^2 = 0.99$) the value of the activation energy of the sorption process was calculated, which was $E_a = 3.9 \pm 0.2$ kJ/mol (Figure 6).

**Figure 5.** Kinetic dependencies of $H_2S$ concentration change on sorption time at different initial concentrations and $T = 298$ K.

**Figure 6.** Linear dependence of the reaction rate constant logarithm on the reciprocal temperature.
The results of the chemical analysis of the studied ore samples after contact with H$_2$S, obtained by the X-ray fluorescence analysis method (Table 3), indicate a significant increase in the sulfur content in the ore, and, as a consequence, a decrease in the relative content of manganese, iron and other elements.

Table 3. Chemical composition of the ore after sorption of hydrogen sulfide (relative percentages).

| Element | MnO  | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO  | MgO  | K$_2$O | SO$_3$ | Impurities |
|---------|------|---------|-------------|-------------|------|------|--------|--------|------------|
| Content, % | 10.19 | 21.67 | 6.47 | 2.36 | 3.74 | 1.34 | 1.48 | 52.48 | 0.27 |

The data on the elemental composition before and after sorption are presented in Table 4.

Table 4. Elemental composition of ore before and after contact with hydrogen sulfide.

| Element | Mg  | Al  | Si  | K  | Ca  | Mn  | Fe  | S  | Σ  |
|---------|-----|-----|-----|----|-----|-----|-----|----|----|
| Mass Content Before Sorption, % | 1.61 | 7.51 | 20.08 | 2.16 | 8.09 | 53.66 | 6.89 | -  | 100 |
| Mass Content After Sorption, % | -  | 4.72 | 7.43 | 0.90 | 3.95 | 65.57 | 6.32 | 11.11 | 100 |

According to the results of X-ray phase analysis of ore samples, after contact with gas, there are no crystalline sulfur-containing phases, while along with quartz hydrated silicate H$_2$Si$_2$O$_5$ and iron (III) oxide, a new phase MnO (OH) appears, which is a hydrated form of manganese (III) oxide Mn$_2$O$_3$ 2H$_2$O. Takanelite (Mn,Ca)Mn$_4$O$_9$ × 3H$_2$O was not found in the ore (Figure 7).

Figure 7. Results of X-ray phase analysis of ore samples after contact with gas.

The formation of elemental sulfur in the composition of ore samples is indicated by the chromatographic analysis results of samples obtained by dissolving with toluene a sulfur-containing substance, which was removed from the surface of the ore after contact with H$_2$S. Based on the phase analysis, it can be assumed that, along with the process of physical adsorption of gas, a chemical redox reaction occurs:

$$2\text{MnO}_2 + \text{H}_2\text{S} = \text{S} + \text{Mn}_2\text{O}_3 + \text{H}_2\text{O},$$

(5)

Physical sorption is caused by the presence of uncompensated interatomic interaction forces on the surface, due to which hydrogen sulfide molecules are attracted. Generally, physical adsorption proceeds at a high rate without activation energy and leads to equilibrium coverage of the active surface of the solid substance.

Temperature range of physical sorption cannot significantly exceed the hydrogen sulfide condensation temperature equal to 212.7. Therefore, with the increasing temperature, the equilibrium coverage will decrease, while there is no such limitation for chemisorption,
it can occur both at low (less than 273 K) and at higher temperatures (more than 273 K). Chemisorption of the reactant, opposed to physical sorption, is proceeding with the involvement of an activated complex characterized by a certain activation energy. The presence of iron (III) oxide in the ore composition can affect the chemical sorption process, contributing to its acceleration due to the generated catalytic effect [15,16].

To determine the effect of iron (III) oxide on the chemical reaction rate, a series of hydrogen sulfide sorption experiments were carried out on iron (III) oxide with a specific surface area of 31 m$^2$/g and a pore size of 4.84 × 10$^{-8}$ m and on a model sample consisting of SiO$_2$, Al$_2$O$_3$ and MnO$_2$ oxides mixture, which does not contain Fe$_3$O$_4$ and quantitatively represents the composition of the studied ore. The specific surface area of 75 m$^2$/g and the pore size of 3.33 × 10$^{-8}$ m of the model sample are practically commensurable with those of real ore samples, which makes it possible to compare their kinetic sorption characteristics. According to the experimental results, iron (III) oxide showed no sorption tendency to hydrogen sulfide. During the experiment phase and H$_2$S concentration changes were not observed. The dependencies of the H$_2$S concentration change on time during sorption on model samples containing manganese (IV) oxide and the rate constant logarithm on reciprocal temperature are shown in Figures 8 and 9.

![Figure 8](image_url)

**Figure 8.** Dependencies of the H$_2$S concentration change on time during sorption on model samples containing MnO$_2$ at different temperatures.

![Figure 9](image_url)

**Figure 9.** Linear dependence of the reaction rate constant logarithm on the reciprocal temperature.
The calculated value of the hydrogen sulfide sorption activation energy on model samples containing manganese (IV) oxide was 18.6 ± 0.9 kJ/mol. The increase in the activation energy is probably caused by the absence of iron (III) oxide in the composition of the sorption material.

According to the Bronsted–Polanyi equation for catalytic processes, the difference between the activation energy of the process in the absence ($E_0$) and in the presence ($E$) of the catalyst is determined by the heat effect of $H_2S$ chemisorption by the catalyst, where $\alpha$ is a constant coefficient for a given reaction and catalyst, varying from 0 to 1:

$$E = E_0 - \alpha \times \Delta H.$$  

(6)

The catalytic conversion of $H_2S$ includes the following stages: physical adsorption, chemisorption, chemisorption of reaction products, physical adsorption of reaction products and proceeds according to the scheme:

1. $H_2S + [\cdot] \rightarrow H_2S_{ads}$
2. $H_2S_{ads} + 2[MnO_2] \rightarrow [Mn_2O_3] + S_{ads} + H_2O_{ads}$
3. $S_{ads} + H_2O_{ads} \rightarrow S + H_2O + [\cdot]$

where $[\cdot]$—free for chemisorption area on the active surface. Therefore, the energy path of the hydrogen sulfide sorption and oxidation process will include three peaks corresponding to three stages of the process. Consequently, for each individual process, the values of the activation energies can be expressed in accordance with the Bronsted–Polanyi rule:

$$E_1 = E_{01} - \alpha \times \Delta H_1$$  

(7)

$$E_2 = E_{02} + (1 - \alpha) \times \Delta H_1 - \alpha \times \Delta H_2$$  

(8)

$$E_3 = E_{03} + (1 - \alpha) \times \Delta H_2$$  

(9)

where $E_{1,2,3}$—is the activation energy of the first, second and third stages of the process with the catalyst participation, $\Delta H_1$ and $\Delta H_2$—chemisorption heats of the initial material $H_2S_{ads}$ and reaction products $S_{ads} + H_2O_{ads}$, $\alpha$—coefficients for the corresponding reaction (5) and catalyst.

According to the Bronsted–Polanyi rule, the activation energy of the first stage will decrease by the hydrogen sulfide chemisorption heat amount of $\Delta H_1$, while the activation energy of the second stage should increase by the chemisorption heat value of the initial substance $H_2S$ due to the formed bonds of adsorbed $H_2S$ with the catalyst and decrease with an increase in the chemisorption heat of the reaction products $S_{ads} + H_2O_{ads}$. The energy of the third stage will increase with an increase in the products chemisorption heat. Therefore, according to the first reaction the hydrogen sulfide sorption rate can be expressed by the equation:

$$v_1 = K_{01} \exp \left( - \frac{E_{01} - a\Delta H_1}{RT} \right) (1 - \theta_1 - \theta_2) = k_1 \exp \left( \frac{a\Delta H_1}{RT} \right) (1 - \theta_1 - \theta_2)$$  

(10)

and the chemical reaction rate is expressed by Equation (11):

$$v_2 = K_{02} \exp \left( - \frac{E_{02} - (1 - a)\Delta H_1 - a\Delta H_2}{RT} \right) \theta_1 = k_2 \exp \left( \frac{a\Delta H_2 - (1 - a)\Delta H_1}{RT} \right) \theta_1$$  

(11)

and thus, the hydrogen sulfide desorption rate is expressed by Equation (12):

$$v_3 = K_{03} \exp \left( - \frac{E_{03} - (1 - a)\Delta H_2}{RT} \right) \theta_2 = k_3 \exp \left( \frac{(1 - a)\Delta H_2}{RT} \right) \theta_2$$  

(12)

where $\theta_1$ and $\theta_2$ are the sections of $Fe_3O_4$ surface, occupied by the chemisorption components of $H_2S$, $S_{ads}$ and $H_2O_{ads}$; $K_{01}$, $K_{02}$, $K_{03}$—rate constants of first, second and third process stages; $k_1$, $k_2$, $k_3$—coefficients independent of $H_2S$, $S_{ads}$ and $H_2O_{ads}$ chemisorption heat.

The system will remain a stationary state if some of its essential characteristics do not change over time or if the formation rate of a system component is equal to its decay rate.
When the stationary state of the hydrogen sulfide sorption process is reached, the total speed of the system will be equal to the speed of each of the conjugate stages:

$$v = v_1 = v_2 = v_3 = k_2 \exp \left( \frac{\alpha \Delta H_2 - (1 - \alpha) \Delta H_1}{RT} \right) \theta_1 = k_3 \exp \left( - \frac{(1 - \alpha) \Delta H_2}{RT} \right) \theta_2$$

from the equality of which we find the values of $\theta_2$ and $\theta_1$ by Equations (14) and (15):

$$\theta_2 = \frac{k_2}{k_3} \exp \left( \frac{\Delta H_2 - (1 - \alpha) \Delta H_1}{RT} \right)$$

$$\theta_1 = \frac{1}{1 + \frac{k_2}{k_1} \exp \left( \frac{\alpha \Delta H_2 - \Delta H_1}{RT} \right) + \frac{k_3}{k_3} \exp \left( \frac{\Delta H_2 - (1 - \alpha) \Delta H_1}{RT} \right)}$$

and express the overall process rate:

$$v = \frac{k_2 \exp \left( \frac{\alpha \Delta H_2 - (1 - \alpha) \Delta H_1}{RT} \right)}{1 + \frac{k_2}{k_1} \exp \left( \frac{\alpha \Delta H_2 - \Delta H_1}{RT} \right) + \frac{k_3}{k_3} \exp \left( \frac{\Delta H_2 - (1 - \alpha) \Delta H_1}{RT} \right)}.$$ (16)

From the conditions $\frac{dv}{d\Delta H_1} = 0$ at $\Delta H_2 = \text{const}$ and $\frac{dv}{d\Delta H_2} = 0$ at $\Delta H_1 = \text{const}$ we find the solutions of this equation:

$$\Delta H_1 = RT \ln \left( \frac{k_2}{k_1} \frac{\alpha}{1 - \alpha} \right) + a \Delta H_2 \text{ and } \Delta H_2 = RT \ln \left( \frac{k_3}{k_2} \frac{\alpha}{1 - \alpha} \right) + (1 - \alpha) \Delta H_1,$$

the substitution of which in Equations (14) and (15) allows to obtain expressions for the section of the catalyst surface $\theta_1$ and $\theta_2$, optimally covered with chemisorbed substances:

$$\theta_1 = \frac{\alpha(1 - \alpha)}{1 - \alpha - \alpha^2} \text{ and } \theta_2 = \frac{\alpha^2}{1 - \alpha - \alpha^2}.$$ (17)

If we assume that the free surface of the catalyst is evenly distributed between $H_2S_{ads}$, $S_{ads}$ and $H_2O_{ads}$, then the values of $\theta_1$ and $\theta_2$ are equal, which is observed at $\alpha = 0.5$ and corresponds to the maximum catalytic reaction rate. To assess the uniform distribution degree of the reactants and reaction products on the Fe$_3$O$_4$ surface, the heat of hydrogen sulfide sorption on the surface of ferromanganese ore was measured. The heat value of the sorption process was: $\Delta H = -69.44 \pm 1.39 \text{ kJ/mol}$.

If the calculated activation energy of sorption on ore samples is taken as the total value of the activation energies of the chemisorption stage, chemical transformation stage, and desorption stage, then the coverage degree of the iron (III) oxide surface with chemisorbed substances can be estimated. According to the calculations by Formulas (6) and (17), the coverage degree values were: $\theta_1 = 0.23$ and $\theta_2 = 0.07$. With these values of the coverage degree, the rate constant ratio of physical sorption and chemical reaction $\left( \frac{k_2}{k_1} \right)$ was estimated, which was $1.25 \times 10^{-14}$, which characterizes chemisorption (redox reaction) as the limiting stage of the process. The Fe$_3$O$_4$ role as a catalyst resides in the electronic conductivity presence due to the element existence in two different valence states, in equivalent positions of the crystal lattice, and the possibility of electron exchange between iron ions (2+) and (3+). The general mechanism of catalyst action in oxidation reactions reside in the simplification of electronic transitions in reacting molecules due to their own electrons. The process begins with the interaction of the solid body electrons with the reacting molecules of hydrogen sulfide, which leads to deformation of the adsorbed molecule and weakening of intramolecular bonds.

The catalytic oxidation of hydrogen sulfide is of interest, first of all, as an effective method for purifying industrial gas emissions from it. In addition, the study of this process is important for the development of the catalysts selective action theory, since the formation
of three sulfur-containing products is possible during the oxidation of hydrogen sulfide: S, \( \text{SO}_2 \) and \( \text{SO}_3 \). The use of ferromanganese materials for the sulfur-containing gases purification, for which unrefined ferromanganese ore was used in this work, makes it possible to eliminate any losses of \( \text{H}_2\text{S} \) and provide the waste-free process. The adsorbed sulfur is recovered during ore reprocessing into iron and manganese compounds. The method, based on selective catalytic oxidation of hydrogen sulfide from hydrocarbon and metallurgical industrial gases, makes preliminary gas purification from hydrogen sulfide, its concentration and oxidation to sulfurous anhydride unnecessary. The use of manganese and iron (III) oxides has a technological advantage over the currently used titanium and aluminum oxides, which require a constant composition and high specific surface area: the oxidation process of \( \text{H}_2\text{S} \) with manganese oxide is characterized by one-stage and continuous operation, unlike the known Claus method, and mild temperature conditions for the implementation of the process.

The obtained quantitative regularities of the direct catalytic oxidation process of hydrogen sulfide made it possible to estimate the contribution of physical and chemical sorption to the main process of the elemental sulfur formation. The mathematical description of the desorption process, taking into account the conjugated stages of sorption and desorption of all participants of the hydrogen sulfide oxidation process, based on the Bronsted–Polyani theory, can be used to describe any catalytic processes in order to determine the catalytic activity of the catalyst and the fraction of its active surface. Foresight of the catalytic action is the most important task of the catalysis theory.

4. Conclusions

In this work, the kinetic features of the sorption process of hydrogen sulfide, possessed by reducing properties on an inorganic natural ferromanganese material containing crystalline phases of \( \text{FeO} \times \text{Fe}_2\text{O}_3 \), takanelite \((\text{Mn,Ca})\text{Mn}_4\text{O}_9 \times 3\text{H}_2\text{O}\) and quartz \( \text{SiO}_2 \) are determined. The fundamental possibility of effective gas purification process from hydrogen sulfide with the use of inorganic materials with oxidizing properties based on iron and manganese oxides, is shown. The catalytic effect of the iron (III) oxide presence in ferromanganese samples on the hydrogen sulfide sorption process was revealed. The activation energy values of \( \text{H}_2\text{S} \) sorption by ore samples and model samples simulating the composition of ferromanganese material without \( \text{Fe}_2\text{O}_3 \) content, were calculated and amounted to \( 3.9 \pm 0.2 \) and \( 18.6 \pm 0.9 \text{ kJ/mol} \). The \( \text{Fe}_2\text{O}_3 \) presence increases the energy compensation degree of the antibonding bonds by the energy of the formed ones.

The sulfur (IV) and (IV) oxides absence in the gas mixture after sorption and the appearance of elemental sulfur in solid samples were determined by the chromatographic method. The results of X-ray phase analysis demonstrate the appearance of a new hydrated crystalline phase \( \text{Mn}_2\text{O}_3 \times 2\text{H}_2\text{O} \), which is absent in the initial samples. Based on the analysis of the hydrogen sulfide sorption products, the process is expressed by a chemical redox reaction:

\[
2\text{MnO}_2 + \text{H}_2\text{S} = \text{S} + \text{Mn}_2\text{O}_3 + \text{H}_2\text{O}.
\]

According to the results, the measured heat of the \( \text{H}_2\text{S} \) sorption process was \( \Delta H = -69.44 \pm 1.39 \text{ kJ/mol} \), and a limiting stage was established, which is a chemical reaction. The hydrogen sulfide and reaction products distribution degree on the \( \text{Fe}_2\text{O}_4 \) surface was estimated. An unequal coverage degree of the catalyst surface by the chemical reaction components was revealed: the section \( \theta_1 \) occupied by the chemisorption initial component \( \text{H}_2\text{S} \) was 0.23, while the section of the chemisorption reaction products \( \text{S} \text{ads} \) \( \text{H}_2\text{O} \text{ads} \) was only 0.07. The optimum or maximum rate of the hydrogen sulfide sorption process corresponds to the coverage degrees equality \( \theta_1 \) and \( \theta_2 \), which can be achieved by changing the structure of the catalyst, creating the optimal size and shape of its grains.

Thus, the established features of the catalytic process of \( \text{H}_2\text{S} \) sorption by ferromanganese materials contribute to the development of an optimal catalyst for carrying out catalytic reactions on an industrial scale.
Author Contributions: Conceptualization, O.C. and E.C.; methodology, M.P.; software, V.B.; validation, M.P. and O.C.; formal analysis, E.C.; investigation, V.B. and A.F.; resources, O.C. and M.P.; data curation, O.C and E.C.; writing—original draft preparation, O.C. and M.P.; writing—review and editing, A.F.; visualization, V.B. and A.F.; supervision, M.P.; project administration, O.C.; funding acquisition, O.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data is contained within the article.

Acknowledgments: The research was carried out with the involvement of the laboratory facilities of the Saint-Petersburg Mining University Collective Use Center. The authors express their gratitude and appreciation to the staff of the departments of metallurgy and physical chemistry of the Saint-Petersburg Mining University for their attention, help, and support at different stages of writing the article.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Glazev, M.; Bazhin, V. Environmental technologies in the production of metallurgical silicon. In Scientific and Practical Studies of Raw Material Issues; CRC Press: Boca Raton, FL, USA, 2019; pp. 114–119, ISBN 9780367861537.

2. Bykova, M.V.; Pashkevich, M.A. Engineering and ecological survey of oil-contaminated soils in industrial areas and efficient way to reduce the negative impact. In Scientific and Practical Studies of Raw Material Issues; CRC Press: Boca Raton, FL, USA, 2019; pp. 135–142, ISBN 9780367861537.

3. Dubovikov, O.A.; Brichkin, V.N.; Ris, A.D.; Sundurov, A.V. Thermochemical activation of hydrated aluminosilicates and its importance for aluma production. Non-Ferrous Met. 2018, 45, 10–15. [CrossRef]

4. Tarasov, K.A.; Burkat, V.S.; Volkodaeva, M.V. Analysis of the Concentration of Gas-Phase and Solid-Phase Polyaromatic Hydrocarbons in Industrial Emissions from Aluminum Production. Metallurgist 2020, 63, 1227–1236. [CrossRef]

5. Lebedev, A.B.; Utkov, V.A.; Khalifa, A.A. Sintered sorbent utilization for H2S removal from industrial flue gas in the process of smelter slag granulation. J. Min. Inst. 2019, 237, 292–297. [CrossRef]

6. Shcherbakova, N.; Khaitkin, M. City as an Object of Ecological and Economic Researches: The Example of Russian Cities. IOP Conf. Ser. Earth Environ. Sci. 2019, 272, 032119. [CrossRef]

7. Kovshov, S.V.; Skamyin, A.N. Treatment of agricultural wastes with biogas–vermitechnology. Environ. Earth Sci. 2017, 76, 660. [CrossRef]

8. Sutimova, M.A. About the interchangeability of iron-manganese nodules of the Pacific and the Baltic Sea. IOP Conf. Ser. Mater. Sci. Eng. 2020, 919, 062039. [CrossRef]

9. Zhuravskiy, S.V.; Kalenyuk, A.A.; Kartel, N.T.; Tarasenko, Y.A.; Zaitsev, Y.P.; Ivanenko, I.N. Okislitelnaya sorbtsiya serovodoroda. Poverkhnost 2014, 6, 68–82. [CrossRef]

10. Lau, L.C.; MohamadNor, N.; Lee, K.T.; Mohamed, A.R. Adsorption Isotherm, Kinetic, Thermodynamic and Breakthrough Curve Models of H2S Removal Using CeO2/NaOH/PSAC. Int. J. Petrochemical Sci. Eng. 2016, 1, 36–44. [CrossRef]

11. Aslam, Z.; Hussein, I.A.; Shawabkeh, R.A.; Parvez, M.A.; Ahmad, W.; Ihsanullah. Adsorption kinetics and modeling of H2S by treated waste oil fly ash. J. Air Waste Manag. Assoc. 2019, 69, 246–257. [CrossRef] [PubMed]

12. Hong, Y.S.; Zhang, Z.F.; Cai, Z.P.; Zhao, X.H.; Liu, B.S. Deactivation Kinetics Model of H2S Removal over Mesoporous LaFeO2/MCM-41 Sorbent during Hot Coal Gas Desulfurization. Energy Fuels 2014, 28, 6012–6018. [CrossRef]

13. Sharikov, Y.V.; Sharikov, F.Y.; Titov, O.V. Application of heat-flow calorimetry for developing mathematical models of reactor processes. Theor. Found. Chem. Eng. 2016, 50, 225–230. [CrossRef]

14. Bolotov, V.A.; Cheremisina, O.V.; Ponomareva, M.A.; Alferova, D.A. Prospects for the Use of the Sorbent for Purification of Gases from Sulfur-Containing Components on the Basis of Manganese Ore. Key Eng. Mater. 2020, 836, 13–18. [CrossRef]

15. Kadirova, Z.C.; Katsumata, K.; Isobe, T.; Matsushita, N.; Nakajima, A.; Okada, K. Adsorption and photodegradation of methylene blue by iron oxide impregnated on granular activated carbons in an oxalate solution. Appl. Surf. Sci. 2013, 284, 72–79. [CrossRef]

16. Zhang, X.; Dou, G.; Wang, Z.; Li, L.; Wang, Y.; Wang, H.; Hao, Z. Selective catalytic oxidation of H2S over iron oxide supported on alumina-intercalated Laponite clay catalysts. J. Hazard. Mater. 2013, 260, 104–111. [CrossRef] [PubMed]