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ON THE NATURE OF THE INTERACTION OF FERRIC OXIDE AND GERMANIUM DIOXIDE

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The study of the nature of the interaction of iron oxides with germanium oxides is of considerable interest not only from the standpoint of the chemistry and technology of germanium, but is also highly relevant for understanding the geochemistry of this important element. As early as 1933, Goldschmidt ([1]) established an increased content of germanium in iron ores. In recent years, reports have been published on investigations of germanium-bearing iron ores ([2,3]). Little attention has so far been paid to the question of the causes that bring about the concentration of germanium in iron ores, and to the forms in which germanium is retained in them.

However, the well-known method for the quantitative determination of germanium in solutions is based on the interaction of these elements; according to this method, germanium ions present in solution are precipitated on ferric hydroxide ([4]).

The present communication gives the results of investigations, by thermal and X-ray phase analyses, of precipitates obtained by coprecipitation of hydrated ferric oxide with various amounts of germanium, and of mixtures of dry oxides. Experiments on coprecipitation and subsequent study of the precipitates were carried out at molecular ratios $Fe_2O_3 : GeO_2$ of 4 : 1, 3 : 2, 2 : 3, and 1 : 4. From solutions with such oxide ratios, hydrated ferric oxide was precipitated with ammonia or sodium hydroxide. The precipitates obtained were washed with a weak electrolyte solution and with water. The filtrates and wash waters were analyzed for germanium and iron. The amount of germanium in the filtrates and wash waters is given in Table 1. Iron was not detected in the filtrates and wash waters.

Table 1

Germanium content in filtrates and wash waters after precipitation of $Fe(OH)_3$ from solutions with sodium hydroxide and ammonia

Molec. ratio $Fe_2O_3 : GeO_2$	Taken $Fe_2(SO_4)_3 \times 9H_2O$, calculated as Fe_2O_3, g	Taken GeO_2, g	Taken GeO_2, calculated as Ge, g	Found Ge in filtrate and wash waters, g: NaOH	Found Ge in filtrate and wash waters, g: NH_4OH	Ge precipitated on $Fe(OH)_3$, %: NaOH	Ge precipitated on $Fe(OH)_3$, %: NH_4OH
1 : 4	0.63	1.68	1.17	0.1125	0.0690	90.4	94.1
2 : 3	1.25	1.25	0.87	0.0270	0.0245	96.9	97.18
3 : 2	1.88	0.84	0.59	0.0016	0.0011	99.72	99.81
4 : 1	2.50	0.42	0.29	0.0004	0.0001	99.86	99.96

As is evident from Table 1, germanium coprecipitates quantitatively with iron over a very wide range of concentrations. The amount of germanium retained by ferric hydroxide increases regularly with increasing $Fe_2O_3 : GeO_2$ ratio. Somewhat more favorable results with respect to completeness of germanium precipitation were obtained when ammonia was used as the precipitating reagent.

The precipitates of iron oxide hydrate with coprecipitated germanium were dried at 105—110° to constant weight. The color of the precipitates changes smoothly from dark brown for pure $Fe(OH)_3$ to light brown for the mixture with the ratio $Fe_2O_3 : GeO_2 = 1 : 4$. The precipitates obtained were subjected to thermal

Fig. 1

Fig. 2

and X-ray phase analysis. In the thermograms of the precipitates obtained by precipitation with ammonia and caustic soda, an almost complete analogy is observed. The X-ray diffraction patterns (interplanar spacings and line intensities) are given in Table 2.

Table 2

X-ray diffraction patterns of the initial products and their mixtures

Phase $2Fe_2O_3 \cdot 7GeO_2$	Phase $2Fe_2O_3 \cdot 7GeO_2$	Phase Fe_2O_3	Phase Fe_2O_3	Phase GeO_2	Phase GeO_2	Phase $2Fe_2O_3 \cdot 3GeO_2$	Phase $2Fe_2O_3 \cdot 3GeO_2$
I	$\frac{d}{n}\alpha$	I	$\frac{d}{n}\alpha$	I	$\frac{d}{n}\alpha$	I	$\frac{d}{n}\alpha$
8	3,342	4	4,409	1	4,396	7	3,794
6	3,077	6	3,661	2	4,293	6	3,400
10	3,037	5	2,983	5	3,794	7	3,085
9	2,960	3	2,785	10	3,401	4	3,006
7	2,602	10	2,690	2	2,578	9	2,789

Fig. 3

Figure 1: Fig. 3

Fig. 4

Figure 2: Fig. 4

Phase $2Fe_2O_3\cdot7GeO_2$	Phase $2Fe_2O_3\cdot7GeO_2$	Phase Fe_2O_3	Phase Fe_2O_3	Phase GeO_2	Phase GeO_2	Phase $2Fe_2O_3\cdot3GeO_2$	Phase $2Fe_2O_3\cdot3GeO_2$
9	2,518	9	2,525	4	2,471	10	2,606
1	2,324	3	2,441	3	2,374	6	2,523
1	2,260	6	2,199	4	2,263	4	1,945
5	2,036	4	2,023	1	2,163	5	1,874
4	1,859	3	1,859	4	2,055	4	1,737
1	1,735	7	1,832	3	1,486	3	1,693
6	1,692	1	1,759	6	1,714	4	1,652
6	1,650	8	1,692	1	1,558	3	1,576
1	1,601	3	1,631	2	1,517	2	1,421
2	1,575	5	1,593	7	1,449	1	1,330
7	1,549	7	1,477	3	1,428	1	1,288
3	1,470	7	1,448	4	1,376		
8	1,427	1	1,341	1	1,330		
1	1,364	5	1,304	3	1,279		
1	1,335	4	1,255	3	1,246		
1	1,289	1	1,222	1	1,208		
1	1,255	1	1,209	2	1,154		
		4	1,186	1	1,141		
		5	1,158	2	1,096		
		6	1,135	2	1,086		
		6	1,099	3	1,076		
		7	1,052	1	1,059		
		3	1,043	4	1,034		
		4	0,987	3	1,028		
				8	1,006		

In the thermogram of ferric oxide hydrate (Fig. 1), in addition to the usual dehydration effect at 150-200°, an exothermic effect is observed at a temperature close to 500°. It should be noted that in the work of Chalyi et al. (^5) this effect was not recorded.

Fig. 3

Fig. 4

Apparently, it corresponds to crystallization of Fe_2O_3, which is confirmed by the data of X-ray phase analysis. The X-ray pattern of precipitated $Fe(OH)_3$ and calcined at 520° for one hour agrees well with the X-ray pattern of hematite α-Fe_2O_3 (ˆ6). On the thermogram of GeO_2, only two dehydration effects are noted (from 100 to 200°).

The thermogram of the mixture $Fe_2O_3 : GeO_2$ $1 : 4$ has an endothermic dehydration effect (200–230°) and two exothermic effects (620 and 800°) (Fig. 2). The X-ray pattern of the product calcined at 620° shows the lines of GeO_2 and the lines of a new phase, while after calcination at 800° new lines appear, different from those of GeO_2 and Fe_2O_3. Since the second X-ray pattern contains no lines of any other phases, it may be assumed that the composition of the phase crystallizing at this temperature corresponds to the compound $Fe_2O_3 : GeO_2$ $1 : 4$. Taking into account that, in preparing this mixture, only 90% of the germanium taken was precipitated (see Table 1), the composition of the compound obtained may be assigned the formula $2Fe_2O_3 \cdot 7GeO_2$.

The thermogram of the precipitate of composition $Fe_2O_3 : GeO_2$ $2 : 3$ (Fig. 3) has endothermic effects (200 and 400°) and exothermic effects (610 and 680°). In addition, a decomposition effect is noted at 910°. The X-ray pattern of the product calcined at 200 and 400° has no lines. Distinct lines appear only after calcination at the temperatures of the last two effects. At 680° the same phase crystallizes as at 620° in the mixture $Fe_2O_3 : GeO_2$ $1 : 4$. From the X-ray pattern it follows that this phase crystallizes practically without impurities, i.e., it is the compound $2Fe_2O_3 \cdot 3GeO_2$. At 910° a phase crystallizes with lines close to those of the phase $2Fe_2O_3 \cdot 7GeO_2$, and lines of the Fe_2O_3 phase appear. On this basis it may be assumed that, in the temperature interval up to 400°, hygroscopic, crystallization, and hydrate water is removed from the product of composition $2 : 3$. In the region 630–680°, a germanate of composition $2Fe_2O_3 \cdot 3GeO_2$ crystallizes, and in the region 900–910° this germanate decomposes with the formation of the germanate $2Fe_2O_3 \cdot 7GeO_2$ and Fe_2O_3.

The thermograms (Fig. 4) and X-ray patterns of mixtures of compositions $2 : 3$ and $4 : 1$ differ little from one another. The exothermic effect of formation of the germanate $2Fe_2O_3 \cdot 3GeO_2$ (which is established from the X-ray patterns of the products) in the mixture with the higher iron content has a temperature 100° lower; the decomposition effects of this germanate, with formation of the germanate $2Fe_2O_3 \cdot 7GeO_2$ and Fe_2O_3, lie in the same temperature region (910–915°).

The proposed composition of the germanates and their relative stability differ somewhat from the compounds described in the work of Zvorykin et al. (^{7}), which may be explained by different experimental conditions.

Mixtures of dry oxides, taken in the same ratios, were calcined at 700 and 900° for 6–12 h. X-ray patterns of the calcination products show lines only of Fe_2O_3 and GeO_2. Thermograms of these mixtures show no effects except dehydration effects. Hence it may be concluded that, under these conditions, no interaction of the oxides occurs.

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