SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

Mechanism of Reaction between Cobalt(II) Oxide and Ammonium Chloride

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Abstract—A reaction between cobalt oxide and ammonium chloride was studied. A possible mechanism of this reaction was determined by TGA and DSC. The reaction products were identified by IR spectroscopy, chemical and XRD analyses. A multistage mechanism was established for reaction between cobalt oxide and ammonium chloride. Cobalt chloride was determined to be the final product; the reaction occurs via the formation and decomposition of $(NH_4)_3CoCl_5$, $(NH_4)_2CoCl_4$, and NH_4CoCl_3 .

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Naturally occurring cobalt is represented by oxidized and sulfide ore species. Copper-nickel sulfide ores, in which cobalt occurs in the form of CoS, are the major sources of cobalt mining and production. Oxidized nickel ores with cobalt contents of $\sim 0.1\%$ are used less frequently. The process flowsheets that are currently used in industries do not ensure complete cobalt recovery [1, 2]. The research focused on the development of chemical methods for enrichment of polymetal ores is now underway. It is proposed that the possibility of using ammonium chloride as an agent for chlorinating cobalt-containing ores be considered.

Silicon, iron, nickel, and calcium oxides are the macrocomponents of oxidized nickel ores; their reactions with ammonium chloride were studied earlier [3].

Under normal conditions, ammonium chloride is a solid non-corrosive compound. At temperatures above >338°C NH₄Cl is decomposed into gaseous ammonia and hydrogen chloride, escaping the melting stage. The chlorinating properties of ammonium chloride are determined by the difference between the diffusion rates of chloride and ammonium sublimation products.

The vapor pressure of ammonium chloride over a solid at 300°C can be as high as 3 kPa [4]. Upon cooling, the sublimate desublimes into crystalline ammonium chloride. Thus, the range of working temperatures where ammonium chloride is converted from an inert compound into a strong chlorinating agent is appreciably narrow $(300-340^{\circ}C)$.

The chlorination of raw materials with ammonium chloride occurs during batching and heating at 300–340°C. As a result, the valuable components of the ore raw material are converted into chlorides, which subsequently undergo aqueous leaching. Burden rock (silica and alumina) does not interact with ammonium chloride.

The literature contains the results of studies on the reaction between ammonium chloride solutions and cobalt chloride and the isolation of compounds $(NH_4)_2CoCl_4$ from solutions into like crystalline phase [5]; however, these processes belong to the methods of analytical chemistry and are inefficient in large-scale technologies for the extraction of cobalt compounds.

This concerns the solid-phase sintering of ammonium chloride with cobalt(II) oxide and the mechanism of reaction between cobalt(II) oxide and ammonium chloride with the goal of calculating the weight of the opening agent and identifying the reaction products, since ammonium chlorocobaltates, cobalt ammiacates, and cobalt chloride can potentially be formed in this reaction [5, 6].

EXPERIMENTAL

In order to determine the mechanism of the reaction between cobalt oxide and ammonium chloride, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out on an SDT Q600 TGA/DSC/ DTA analyzer equipped with TA instruments Universal V4.2E software (balance sensitivityof 0.1 µg; DSC noise level of $\leq 4 \mu$ W); temperature range of 20–600°C; inert atmosphere (argon flow); heating rate of 5 K/min. The mixture of 13.7 wt % CoO + 86.3 wt % NH₄Cl was used.

RESULTS AND DISCUSSION

The reaction between cobalt(II) oxide and ammonium chloride begins at 181°C (Fig. 1). The product cannot be identified in the 181–264°C range because of being strongly diluted with excess ammonium chloride. Therefore, we conventionally assume that the composition of the product in this temperature range is described by the formula $CoCl_2 \cdot nNH_4Cl \ (n \ge 1)$,



Fig. 1. Thermogravimetric analysis (1) and differential scanning calorimetry (2) for the reaction between CoO and NH_4CI .



Fig. 2. IR spectrum of the reaction product of CoO with NH_4Cl obtained at 260°C.

where *n* depends on the excess ammonium chloride. An endotherm corresponding to the decomposition of the compound that is conventionally denoted as $CoCl_2 \cdot mNH_4Cl$ appears on the DTA curve at 289°C. Further heating results in a weight loss from $CoCl_2$.

Table 1. Results of chemical analysis of the reaction product of NH_4Cl with CoO

Co: Cl: NH ₄	Content, wt %				
ratio	Со	Cl	$\rm NH_4$		
1:5.84:3.84	17.6	61.8	20.6		

The possible mechanism of the reaction can be represented by the following scheme:

$$\begin{array}{c} \text{CoO} + \text{NH}_{4}\text{Cl} \\ \xrightarrow{181^{\circ}\text{C}} & \text{CoCl}_{2} \cdot n\text{NH}_{4}\text{Cl} \\ \xrightarrow{265^{\circ}\text{C}} & \text{CoCl}_{2} \cdot m\text{NH}_{4}\text{Cl} \xrightarrow{289^{\circ}\text{C}} & \text{CoCl}_{2} \end{array}$$

In order to identify $\text{CoCl}_2 \cdot n\text{NH}_4\text{Cl}$, excess ammonium chloride was sintered with cobalt oxide; the reaction was carried out until gaseous products of the reaction (ammonia and water) stopped being released at 260°C.

The product of reaction between ammonium chloride and cobalt(II) oxide obtained at 260°C in excess NH_4Cl was studied by IR spectroscopy.

IR spectra were recorded on a NICOLET 6700 Thermo Electron Corporation Fourier-transform spectrometer within wavenumbers of $50-4000 \text{ cm}^{-1}$; the allowable error of the wavelength scale was $\pm 0.5 \text{ cm}^{-1}$. The samples to be measured in the $400-4000 \text{ cm}^{-1}$ range were pelletizing with KBr (the ratio between the compound under analysis and KBr was 1/300). In the $50-400 \text{ cm}^{-1}$ range, the measurements were carried out in Nujol.

In the IR spectrum of the product of reaction between CoO and NH₄Cl (Fig. 2), there are absorption bands that are characteristic for ammonium ion NH₄⁺ (3146, 3035, 2809, and 1404 cm⁻¹), water of crystallization (3600–3750 and 1602 cm⁻¹), and M–Cl (605, 311, and 176 cm⁻¹).

Based on the IR spectrum of the chlorine-containing cobalt product obtained at 260°C, one can assume the presence of unbound ammonium chloride, which can be attributed to excess NH_4Cl used in the synthesis and the presence of ammoniate complex and cobalt chloride. Additional studies (chemical and X-ray diffraction analyses) were carried out to unambiguously identify the composition of the product.

The forms in which $\text{CoCl}_2 \cdot n\text{NH}_4\text{Cl}$ is present (ammonium chlorocobaltate, cobalt ammoniate, and cobalt chloride) were determined by chemical analysis for unbound NH_3 groups.

The content of chloride ion was determined by titration with standardized $AgNO_3$ solution in the presence of K_2CrO_4 as an indicator. The cobalt content was determined on an ICAP 6300 DUO inductively coupled plasma atomic emission spectrometer. The ammonium ion concentration was determined photometrically using the absorption spectrum of the colored complex of the Nessler reagent with ammonium ion.

According to the results of chemical analysis of $CoCl_2 \cdot nNH_4Cl$ (Table 1), the Co : Cl : NH_4 ratio is 1 : 5.84 : 3.84, which indicates the absence of excessive ammonium. Based on the fact that the product contains excessive ammonium chloride, a conclusion is made that the chlorine-containing product is a mix-

$(CoO + NH_4Cl)$ sample prepared by sintering at 260°C		(NH ₄) ₃ CoCl ₅ [26-0642] [7]		NH ₄ Cl [07-0007] [8]	
d, Å	I, %	d, Å	I, %	d, Å	I, %
7.8690	9	7.8565	79		
6.2518	8	6.3554	10		
4.9489	9	4.9839	59		
3.8780	19			3.8733	25
3.1622	8	3.1728	99		
3.0167	9	3.0225	59		
2.9035	7	2.9093	59		
2.741	100			2.7420	99
2.4754	6	2.4799	59		
2.3745	7	2.3647	30		
2.2365	12			2.2400	4
1.9358	11			1.9405	8
1.8148	8	1.8275	10		
1.7323	10			1.7344	6
1.5815	21			1.5832	25
1.3685	7			1.3711	6

Table 2. Results of XRD of the reaction product of ammonium chloride with cobalt(II) oxide obtained at 260° C

 Table 3. Results of XRD of the decomposition product of ammonium tetrachlorocobaltate

(NH ₄) ₃ CoCl ₅ decomposition product		NH ₄ CoCl ₃ [18-0089] [9]		(NH ₄) ₂ CoCl ₄ [31-0045] [10]	
<i>d</i> , Å	I, %	d, Å	I, %	d, Å	I, %
6.3097	33			6.2560	35
6.0702	78	6.0439	99		
5.2285	100			5.1840	45
4.6431	39			4.6137	16
4.2455	28	4.2579	4	4.2130	10
3.9838	22				
3.6374	41			3.6228	20
3.4910	30	3.4850	8		
3.2557	26			3.2328	20
3.1536	41			3.1527	99
3.0089	46	3.0064	8	2.9976	18
2.8900	22				
2.7803	52			2.7693	35
2.7009	57	2.6982	45		
2.6003	24			2.6160	3
2.4933	25			2.4821	10
2.3614	25			2.3569	3
2.2814	35	2.2828	18	2.2777	12
2.2214	22			2.2188	2
2.1341	33			2.1256	3
2.0852	22			2.0806	12
2.0538	23			2.0407	10
1.9519	24			1.9476	8
1.8855	26	1.9095	2	1.8856	10
1.8192	31	1.8185	6	1.8144	10
1.7689	21			1.7684	20
1.7405	29	1.7434	12		
1.7132	25			1.7084	15
1.6730	27	1.6744	10		
1.6005	21	1.6132	2		
1.4635	21	1.4636	4		

ture of $CoCl_2$ and NH_4Cl or ammonium chlorocobaltate and NH_4Cl .

X-ray powder diffraction analysis was carried out on a DRON-3M instrument equipped with a copper anode (I = 25 mA, V = 35 kV).

The powder pattern of the product of reaction between NH_4Cl and CoO (Table 2) indicates that ammonium pentachlorocobaltate (NH_4)₃CoCl₅ is the major component. The product contains unbound ammonium chloride.

The product of solid-phase sintering of ammonium chloride and cobalt(II) oxide $CoCl_2 \cdot nNH_4Cl$ was kept for 3 h at 280°C; X-ray powder diffraction analysis of the residue was subsequently carried out. The analysis demonstrated two compounds: ammonium trichlorocobaltate and ammonium tetrachlorocobaltate (Table 3).

Thus, according to TGA, NH₄Cl starts reacting with CoO at 180°C; cobalt chloride is the final product of the reaction. Based on the results of chemical analysis, X-ray powder diffraction, and IR spectroscopy, we may claim that the reaction between cobalt oxide and ammonium chloride occurs via the formation of ammonium pentachlorocobaltate. The decomposition of $(NH_4)_3CoCl_5$ is stepwise and occurs via $(NH_4)_2CoCl_4$ and NH_4CoCl_3 formation. Based on the results of the above study, the following scheme of the reactions between cobalt oxide and ammonium chloride may be suggested:

$$CoO + NH_4Cl$$

$$\xrightarrow{181^{\circ}C} (NH_4)_3CoCl_5$$

$$\xrightarrow{T} (NH_3,-H_{Cl}) (NH_4)_2CoCl_4$$

$$\xrightarrow{T} (NH_4,-H_{Cl}) (NH_4)_2CoCl_4$$

$$\xrightarrow{T} (NH_4,-H_{Cl}) (NH_4)_2CoCl_3$$

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