

# TECHNOLOGY OF SEPARATION OF CARBON NANOTUBES FROM NATURAL FERRIFEROUS MANGANESE CATALYSTS WITH THE AID OF AGENTS MADE OF ACETYLENE ALCOHOLS

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## ABSTRACT

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### Key words:

manganese (ferriferous manganese) ore, hydrogen sulfide, adsorbents, syngas, carbon nanotubes, acetylene alcohols, foaming agent, flotation

One of the most promising ways of enhancing value of low-grade manganese (ferriferous manganese) ores is their utilization in cleaning treatment of process gases in the capacity of synthetic scavengers, adsorbents and catalysts, or as a feed stock.

It has been found that in the course of high-temperature removal of sulfur-bearing compounds from process gases using low-grade manganese (ferriferous manganese) ores as adsorbing agents, carbon nanotubes are generated on the adsorbent. The use of the natural ferriferous manganese catalyst for cleaning treatment of process gases and for carbon nanotubes production, and the follow-up re-use in purification circuits or in metallurgy allows enhancing profitability and ecological properties of the final product. Searching for new methods to produce low-cost carbon nanotubes is of interest both for applied and basic science.

A carbon-catalyst composite obtained in the course of decomposition of carbon-bearing gases with the aid of ferriferous manganese ore at a temperature of 850 °C was analyzed. The catalyst was made of ferriferous manganese ore of Porozhin deposit, which exhibited the highest sorption activity in accordance with the evidence of the previous research findings on the use of manganese (ferriferous manganese) ore in the capacity of a catalyst in production of nano-carbon materials. It was found that samples contained carbon nanotubes after catalytic decomposition of methane. The samples contained single-layer and multilayer carbon nanotubes, and chains of carbon nanotubes. Mass fraction of the carbon phase was 32%. The objective was to qualitatively separate the generated carbon structures and the natural catalyst.

Actual separation of carbon nanotubes and catalysts in the world involves grinding, high temperature oxidation owing to different oxidabilities of allotropic forms of carbon, and chemical dissolution of a catalyst in acids. The drawbacks of these methods are irretrievable loss of a catalyst and deterioration of properties of carbon nanotubes.

The research accomplished by Ryabov Yu.V. and his fellows revealed high efficiency of carbon separation from fly ash of coal-fired electric power plants by flotation. The collecting agent was kerosene and the foam maker was pine oil and agents T-66 and T-80. The versatility of properties of acetylene alcohols-based agents DMIPEC and DC-80 enabled presuming foam separation of generated carbon nanotubes from the catalyst bottom layer with the use of these agents only (without kerosene). It was found that nonionic acetylene alcohols-based agents DMIPEC and DC-80 acted as efficient foaming and collecting agents both in flotation of nonferrous metals and carbon-bearing materials of coking coal and carbon nanomaterials. This article proposes a method of foam separation of carbon nanotubes, synthesized with the aid of natural ferriferous manganese ore catalyst, into flotation froth.

From the test data, the best yield of carbon nanotubes is obtained with acetylene alcohols-based agent DC-80: the recovery in carbon concentrate reaches 80–90%.

On the strength of the testing results, the technology of separation of carbon nanotubes from natural ferriferous manganese catalysts with the use of agents made of acetylene alcohols has been developed.

This technology allows extraction of carbon nanotubes in concentrate in the form of powder intended for the subsequent use in modification of composite materials with a view to improving their useful quality and extending operational life of modernized production. Also, carbon concentrate can be used in agglomeration and blending of crushed waste manganese ore for production of ferromanganese. This factor, in its turn, will reduce the cost of ferromanganese.

## Introduction

A principal drawback of manganese supply in Russia is the predomination of poorly commercialized rebellious carbonate ores. Generally, manganese content of ore deposits in Russia is low, making 20.14%. None of such deposits is run on a commercial scale despite continuous striving toward possession of native sources of manganese supply for ferrous metallurgy. In the last five years, manganese ore production has been below 100 thousand tons although the demand is at the level of 1 Mt.

Domestic production is incapable to meet the demands of the Russian industry. In recent years, Russia's import and export of ferromanganese are approximately equal (50–60 thousand tons a year). Import from Norway, France, Ukraine and the Republic of Korea makes 30%.

One of the most promising ways of elevating value of low-grade manganese (ferriferous manganese) ore is the use of this kind ore instead of synthetic adsorbents, scavengers and catalytic agents, or as a feedstock in circuits of process gas cleaning treatment.

The scope of the research work [1] aimed at development of engineering solutions on using natural high-temperature ferromanganese chemisorption agents of hydrogen sulfide in large-scale combined-cycle plants of coal gasification encompassed manganese and ferriferous manganese ore from such deposits as Nokolaev, Porozhin, Askiz, Vandan and Polyarnoe. All tested ore samples exhibited capability to adsorb hydrogen sulfide from gas flow at a high temperature of (500 °C). Porozhin ore demonstrated the highest adsorption capacity [2, 3]. The ability of such adsorbents to remove hydrocarbon sulfide and methyl mercaptan from gas emissions is vital for many industries

(fuel-and-energy industry, paper-and-pulp industry, etc.). This ore kind may be of one-time or multiple use when included in the mentioned technology circuits.

### Experimental research

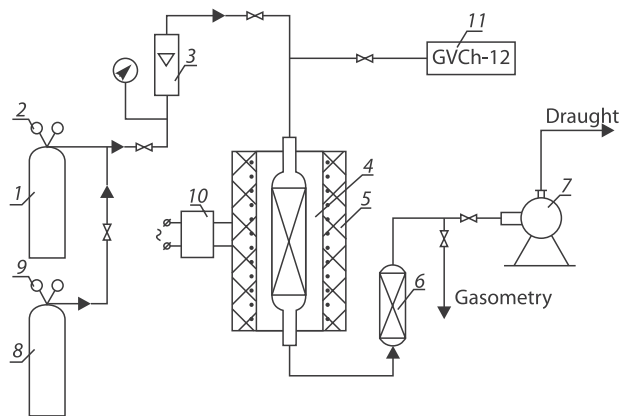
The experimental research undertaken by the Institute of Mineral Resources, Technological Institute and the National University of Science and Technology has shown that manganese ores can find independent application as natural removers of sulfur from gases and in production of carbon nanotubes [4].

The tests were carried out on 4 samples of catalyst ore from Porozhin deposit, with different iron content (from 3 to 19 mass percent) and manganese content (from 13 to 42 mass percent), and bearing  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{TiO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{Na}_2\text{O}$ .

The tests used a plant with hydrogen generation for preliminary recovery of ore–catalyst. The scheme of the plant is presented in **fig. 1**. The plant consists of a chemical reactor (4) placed in a furnace (5), containers of initial syngas (1) and nitrogen (8) and hydrogen generation system GVCh-12 (11). After preliminary recovery by hydrogen, the gas mixture, simulating syngas, is fed from the container (1) via a reduction reducer (2) to the chemical reactor (4) filled with a test material heated to a preset temperature in the electric furnace (5). Gas discharged from the reactor through a filter (6) is forwarded to chromatographic analyzer Gazokhrom-2000 to determine concentrations of  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{CO}$ . Gas flow rate at the inlet and outlet of the chemical reactor is assessed by a gas flowmeter (3) and wet-gas meter GSB-400 (7), respectively. Exit syngas is released in an exhaust system.

Before placement in the chemical reactor, a test material was weighed on an analytical scale together with fine-grained quartz meant for making a bottom layer and for gas distribution in the reactor. Air was displaced from the system using nitrogen from the container (8), and then the material was recovered by hydrogen from the hydrogen generation system (11) at a temperature raised from  $300^\circ\text{C}$  to the test temperature range  $750\text{--}880^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}$  per minute. The mass of the recovered sample was determined in a separate experiment on recovery of catalytic agent without subsequent feed of the simulative gas. After hydrogen feed was completed, initial syngas was directed to the recovered catalyst. The test was carried out for 2–3 hours and longer, and was ended when the composition of the mixture at the reactor outlet stabilized. Then, passivating treatment of the material was undertaken within an hour, at a temperature of  $300\text{--}400^\circ\text{C}$  to avoid inflammation of pyrophoric metal powder.

In the course of the experimental removal of hydrogen sulfide from syngas by the high-temperature treatment



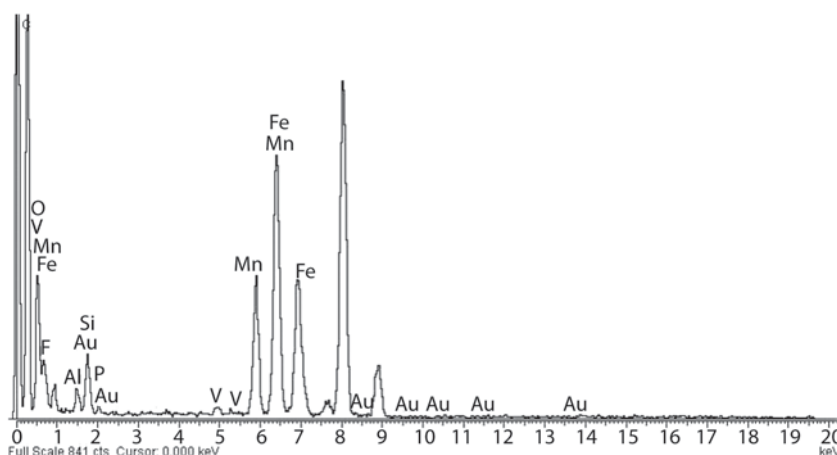
**Fig. 1. Circuit of experimental plant to examine the process of methane decomposition down to nanostructured hydrogen using natural catalysts:**

1 — container with initial syngas (a check mixture); 2, 9 — reduction reducers; 3 — electronic-type gas flowmeter; 4 — chemical reactor; 5 — furnace; 6 — filter; 7 — wet-gas meter; 8 — nitrogen container; 10 — laboratory autotransformer; 11 — hydrogen generation system

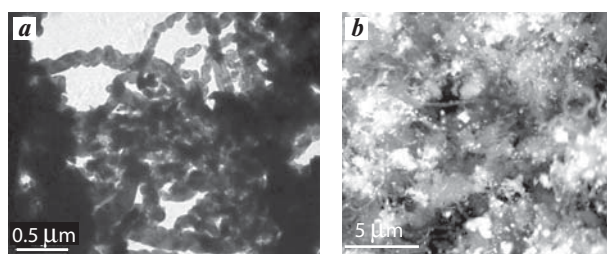
using ferriferous ore–adsorbent, it became evident that no all iron- and manganese-containing ores were applicable to sulfur removal from the viewpoint of preservation of gas heat. The reason was the by-reactions between recovery components of syngas and metallic oxides contained in ore.

The element analysis of the resultant sample treated under the temperature of  $850^\circ\text{C}$  shows the presence of considerable amount of hydrocarbon in the initial catalysts (round 32% of total mass of the material). The outcome of the X-ray spectral analysis of this sample is given in **fig. 2**. The spectrum contains pure line of hydrocarbon, and lines of iron and manganese.

Judging from the presence of hydrocarbon in the samples and based on the review of the related literature [5, 6], it has been inferred that under definite conditions of carbon-bearing gas pyrolysis, it is possible to produce nanostructural carbon—nanotubes and nanofibers, while ore containing compounds of iron and manganese may be a catalyst of chemical settlement of carbon.



**Fig. 2. Spectrum pattern of the catalytic methane decomposition product**



**Fig. 3. Electron micrographs of carbonic structures:**  
*a* — with TEM; *b* — with SEM

The investigation into occurrence of a carbon structure in a ferriferous composite involved scanning electron microscopy (SEM) on microscope PROX PHENON (Netherland) and transmission electron microscopy (TEM) on high-resolution microscope Tecnai-12 (USA). The sample contained high-grade carbonic nano-structured material, mostly nanotubes 500–6000 nm in length, with a diameter of 100–300 nm. The carbonic nanotubes were both single-layer and multilayer (SLNT and MLNT, respectively), and there also were chains of interconnected carbonic nanotubes and nanofibers (fig. 3).

Thus, it has been found that ferriferous ore can serve both adsorbent in process gas cleaning and catalyst in production of carbonic nanomaterials that are more valuable than the original ferriferous ore, which will eventually improve economic performance of mining and processing plants in case of large tonnage production.

The next stage of the research was aimed to separate carbon nanotubes from the underlying catalyst. Carbon nanotubes differ from the other carbonic species by particle size, oxidation susceptibility, conductance, density and surface properties, etc.

Carbon nanotubes are made-up: they are composed of atoms of crystalline allotropic carbon and look like cylindrical crystals. Carbon nanotubes possess unique mechanical, optical and electric properties, exhibit high bending elasticity, while ultimate stress limit of single-layer carbon nanotubes makes 45 GPa [7].

Synthesis of carbon nanotubes is possible through [8]:

- sublimation and desublimation of mineral carbon (electric arc, ablation by laser, sun light or Joule heat as concentrators);

- decomposition or chloration of carbides;
- decomposition or pyrolysis of carbon-bearing gases.

On generation of carbon nanotubes, growth centers of nanotubes appear on the surface of a catalyst, and nanotubes are epitaxial connected with the catalyst, i.e. there arises a nanotube–catalyst composite where nanotubes make unified whole with the catalyst. To produce standard quality carbon nanotubes, it is required to separate them from a catalyst, without much damage, to an individual product with minimized admixtures.

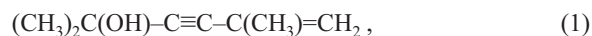
Separation of carbon nanotubes, mineral carbon and amorphous carbon involves grinding, high temperature oxidation, in view of the different oxidation abilities of allotropic carbon species, and dressing based on differ-

ent size and density of particle, e.g. centrifugation. The known approaches to separation of carbon nanotubes and impure mineral carbon are extremely complicated and need much expenditures [9].

Carbon nanotubes are mostly separated through dissolution of catalysts with acids and their mixtures under heating, or in combination with ultrasonic treatment, followed by washing of nanotubes from salts [10]. Major drawbacks of this method are destructive effects of strong acids on walls of carbon nanotubes and generation of many undesirable oxygen-bearing active groups [11]. Metal particles of a catalyst encapsulate inside a tube, are inaccessible for reagents and dirt the product. Implementation of these methods requires high consumption of acids, needs much energy for heating, catalysts are lost irretrievably, which explains high cost of the methods, and, moreover, heated acids exert aggravating effect on health.

The authors of this article propose to separate carbon nanotubes and ferriferous catalysts by flotation in view of the hydrophobic surface of carbon structures. The reagent mode is set by analogy of agents involved into flotation of nonferrous metals and coal. The study [12] reports the data on flotation tests of copper and copper–zinc stock samples in the Northern Urals and Kazakhstan, samples of copper–nickel ore from the Kola Peninsula and coals from Neryungri Preparation Plant. The studies shows that reagents based on higher aliphatic alcohols  $C_7$ – $C_{12}$  and collecting-and-foaming agents based on acetylene alcohols such as DMIPEC and DC-80 exhibit higher efficiency both in flotation of nonferrous metals and coals as against kerosene, MIG-4E, MIBK or T-92.

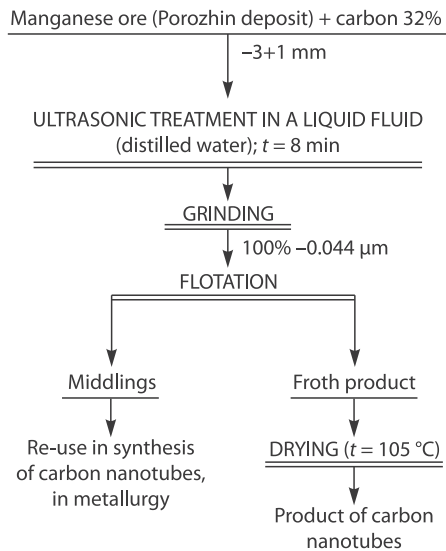
The flotation agent of dimethyl (isopropenyl acetylenyl) carbinol DMIPEC is an auxiliary collecting agent with foaming capacity. This agent is produced from direct interaction of acetylene and acetone and from further dehydration of the product at the stage of its rectification [13]. The general formula of the reagent is:



Flotation agent DC-80  $(CH_3)_2C(OH)-C\equiv CH$  is a lemon-color, slightly hydrocarbon scented and nontoxic liquid. Structurally, this is an individual compound resulting from direct interaction of acetylene and acetone and from further dehydration of the product at the stage of its rectification.

Efficiency of non-ionic collecting-and-foaming agent DMIPEC has been proved in flotation of nonferrous metal sulfides (copper, nickel, zinc, lead) and gold-bearing sulfide ores in Russia (Ural Mining Metallurgy, Norilsk Nickel), Kazakhstan and Chile. DMIPEC allows higher recovery of useful components, better quality of produced concentrates and improved selectivity at lower consumption as compared with the common foamers.

In coal flotation, this agent acts as a foam enhancer with the collecting abilities; it is taken in amount of 50–100 g/t when combined with another collecting agent and in amount of 120–500 g/t when used individually. The incre-



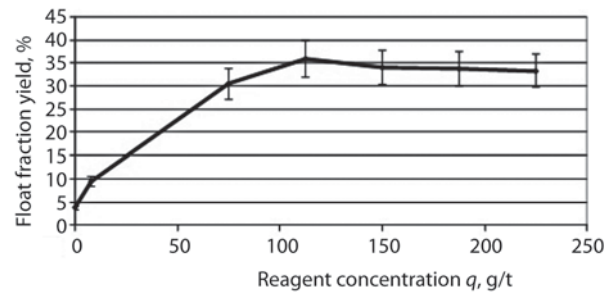
**Fig. 4. Circuit of foam separation of carbon-and-catalyst composite**

ment of coal recovery in concentrate as against check specimens is 3–8%. The tailings have higher ash content [14].

Flotation of oxidized low-caking coal gives satisfactory yield and ash content of concentrate, though the ash content of tailings is low. The flotation results obtained at considerable reduction in the consumption of the reagent are acceptable for the technology in operation at Neryungri Preparation Plant, though duration of the flotation circuit is a little expanded. All tests on flotation of coking coal yield good results [15].

Accordingly, the feedstock used in testing efficiency of separation of carbon nanotubes from a catalyst by flotation—agents  $C_7$ – $C_{12}$ , DMIPEC and DC-80 based on acetylene alcohols—have proved particular potency of acetylene-containing collectors to be the key elements in flotation of hydrophobic substances with relatively hydrophilic surface areas.

The selected test sample of a catalyst made of Porozhin manganese ore after pyrolysis of carbon-bearing gases at a temperature of 850 °C contains 32 mass percent of carbon as follows from the chemical analysis. Initial size of the sample is  $-3+1$  mm, the sample is pre-treated by ultrasound at a frequency of 18.5 kHz (for more efficient disintegration of hydrocarbon tubes and ore matrix) and is ground on an attrition grinder down to a size of  $-0.44$   $\mu\text{m}$ . Then, non-frothing flotation is carried out in a Hallimond tube, using aliphatic alcohols  $C_7$ – $C_{12}$  and acetylene alcohol-based agents DMIPEC and DC-80 (see **fig. 4**). The all-encompassing capabilities of agents DMIPEC and DC-80 enable anticipating their individual applicability to foam separation of carbon nanotubes and underlying catalysts (without kerosene).



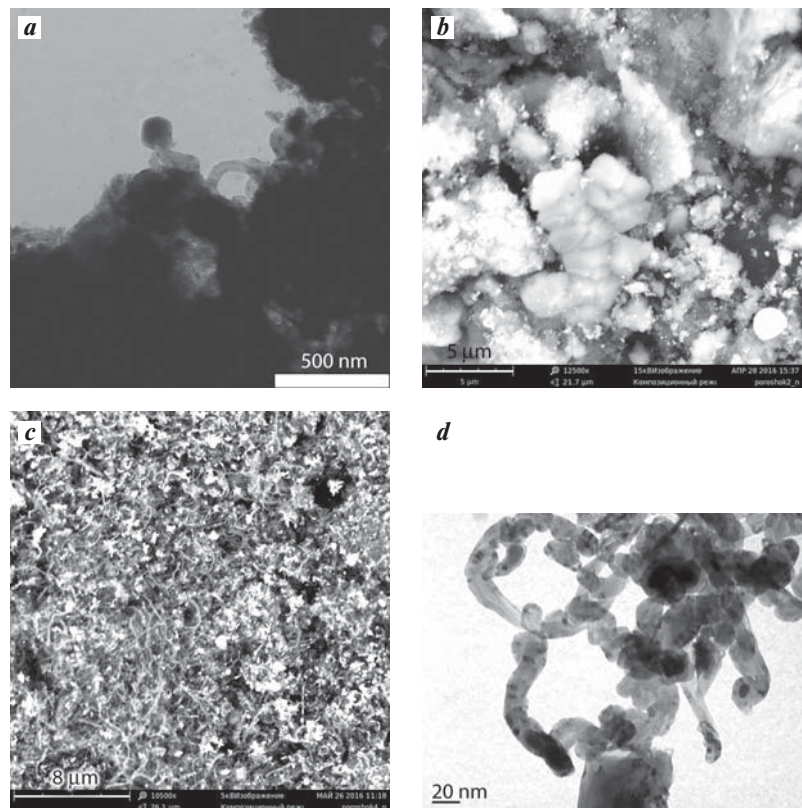
**Fig. 5. Curve of the float fraction yield (%) and agent DC-80 concentration (g/t) in the composite material**

### Discussion of the results

The test results prove efficiency of DC-80 as a collecting agent for naturally hydrophobic carbon nanotubes and a foaming agent in flotation. With DC-80, the yield of the froth product is higher by 33% at the recovery from 85 to 96% as compared with the alcohol solutions of  $C_7$ – $C_{12}$  and agent DMIPEC [16].

The best recovery of nanotubes is the result of flotation with an agent based on isoalkenyl acetylene alcohols. The optimal concentration of agent DC-80 is 120–150 g/t in the range of statistical accuracy (**fig. 5**). Recovery in carbon concentrate is 80–90%.

Thus, manganese ore waste should contain 6–7 mass percent of unseparated carbon to avoid addition of high-priced breeze coke in the circuit of agglomeration and blending of manganese ore waste for production of fer-



**Fig. 6. Micrographs of carbon nanostructures in middlings (a – TEM; b – SEM) and in froth product (c – TEM; d – SEM)**

romanganese. This factor, in its turn, will reduce the cost of ferromanganese.

The micrographs of the transmission electron and scanning electron microscopes (TEM and SEM, respectively) are shown in **fig. 6**.

### Conclusions

1. The process of catalytic decomposition of methane has been studied on model gases with different volume ratios of hydrogen and methane, at a temperature of 800–910 °C and with the catalyst made of ferrous manganese ore with the contents of ferric oxide (III) of 18.9 mass percent and manganese of 12.8 mass percent. Experimental synthesis of carbon nanotubes shows that mass fraction of carbon in the reaction mix is 30–32 mass percent. Further treatment of carbon nanotubes involves their separation from manganese bottom layer. Carbon recovery in concentrate has made 80–90%.

2. The analysis of the catalyst sample made of ferrous manganese ore from Porozhin deposit after tests at 850 °C shows that the sample contains both single-layer and multilayer carbon nanotubes, as well as chains of carbon nanotubes and nanofibers round 500–6000 nm in length with the diameters of 100–300 nm and of high anisotropy.

3. Based on the experimental results, the energy-saving process circuit has been developed, using catalytic decomposition of methane and CO with the aid of natural catalysts, which allows reduction of energy consumption of the production and mitigation of the environmental impact of flotation plants owing to the decrease of content of heavy metals and organic carbon-bearing mass in tailings.

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