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Obtaining Enriched Argon from an Air Mixture by Pressure Swing Adsorption Method

VNIIA
ROSATOM

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INTRODUCTION

The work presents results of the development and experimental investigations of the sampling unit of the automated system for monitoring the ^{37}Ar content in the soil and the surface atmosphere.

METHODS/DATA

The adsorption and separation characteristics of materials (CaA (5A), PSA/VPSA (13XHP) NaX (13X), ZSM-5, and Ag-ZSM-5 zeolites, coconut charcoal and activated charcoal) for air separation and argon extraction from an air sample using the volumetric method have been studied.

START

RESULTS

Adsorption isotherms of the main air components (Ar, N_2, O_2) on these sorbents at room temperature in the pressure range from 0 to 10 bar were obtained. Based on the study, a two-stage system of pressure swing adsorption (PSA) was created to obtain enriched argon.

CONCLUSION

A setup has been developed for investigation of the sorption and separation characteristics of materials.
The sorption and separation characteristics of materials have been studied.
A two-stage PSA system has been developed.

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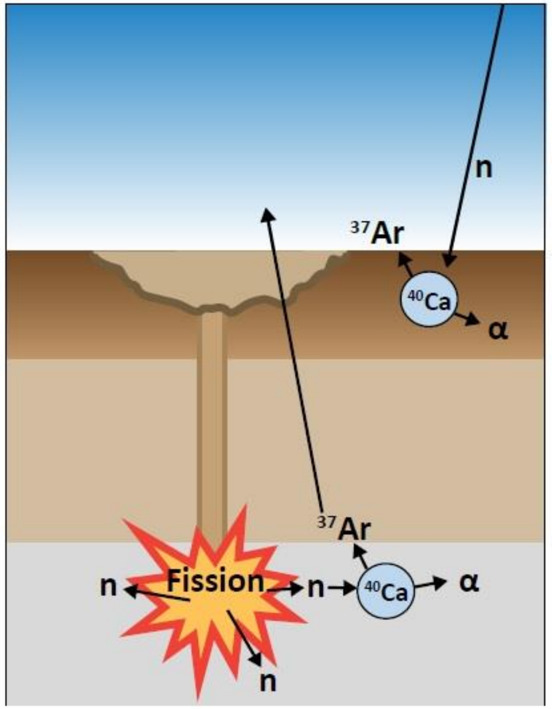
Introduction: Monitoring the content of ^{37}Ar radioactive isotope



Monitoring the content of ^{37}Ar radioactive argon isotope is one of the most important methods for detecting clandestine underground nuclear tests. For a number of years, work in this area supported by the Preparatory Commission for the Comprehensive Nuclear-Test-Ban Treaty Organization (CTBTO).

The ^{37}Ar radiation measurement method used by most monitoring stations is based on low-background proportional counters in which argon gas is a component of the working mixture (10% methane and 90% argon).

- The global atmospheric background level of ^{37}Ar is:

- 0,3 mBq/m^3 [2]

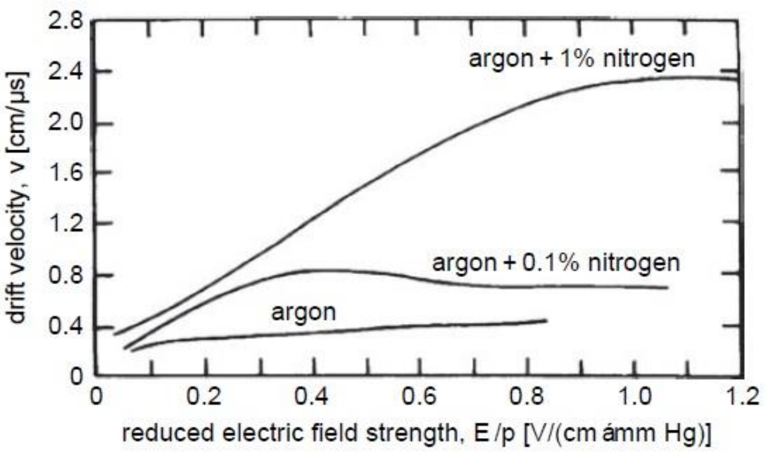
- 1–5 mBq/m^3 [3]

- The underground background level of ^{37}Ar is about 100 mBq/m^3 [2].

Radioactivity measurement system of MARDS [1]

Fig. 3. Image of the radioactivity measurement system.

Introduction: Gas separation system



Drift velocities of electrons in pure argon and in argon with minor additions of nitrogen [4]

<u>The constancy of the electron drift velocity determines the stability of the signal from the proportional counter.</u>

To ensure repeatability of measurements, nitrogen and oxygen must be completely removed from air samples during the argon extraction process. In this regard, an urgent task is to find an effective method for extracting argon from soil gas, concentrating and purifying it for the purpose of further analysis for radioactivity.

Sampling unit	Processing unit	Detection unit
Sampling and concentration	**Purification**	**Measurement**
0,93% Ar (Vol.)		**> 99,9% Ar (Vol.)**

Advantages and disadvantages of methods for air separation and argon production

Method	Rectification [5]	Low temperature adsorption [6]	Pressure swing adsorption (PSA)
Simplicity of design	−	+	+
Low energy consumption	−	−	+
High specific productivity	+	+−	+−

Objectives

1. Development of a setup for investigation of the sorption and separation characteristics of materials for argon extraction and processing.

2. Study of the sorption and separation characteristics of materials for air separation and argon extraction from an air sample in the pressure range from 0 to 10 bar at room temperature.

3. Development of a PSA system on its basis for obtaining enriched argon.

Volumetric method

The state equation [7]:

$$pV = \nu RT$$

where p is the gas pressure, V is the gas volume, ν is the number of moles of the substance, T is the absolute temperature, R is the universal gas constant (8.31 J/mole K).

$$p_0 V_0 = \nu_0 RT \quad (1)$$

$$p_1 (V_{fr} + V^*) = \nu_1 RT \quad (2)$$

where V^* is the volume of the pipeline.

$$p_2 (V_{fr} + V^* + V_0) = \nu_2 RT \quad (3)$$

Due to the assumption of the absence of helium sorption in the system:

$$\nu_2 = \nu_0 + \nu_1 \quad (4)$$

From formulas (1)-(4), an expression is obtained for the free volume V_{fr}:

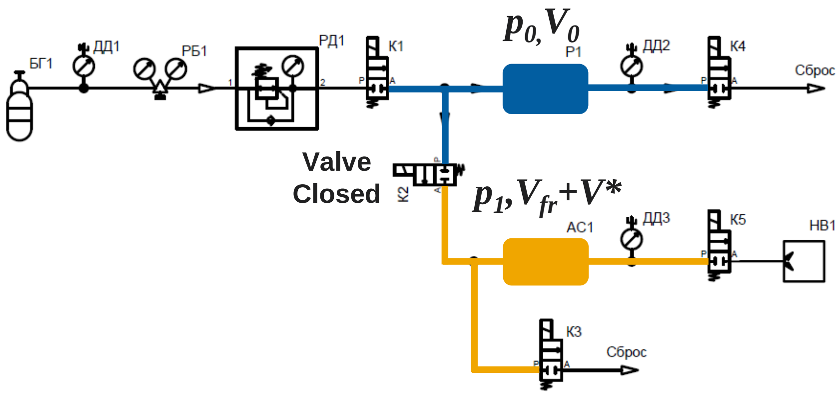
$$V_{fr} = \frac{p_2 - p_0}{p_1 - p_2} V_0 - V^* \quad (5)$$

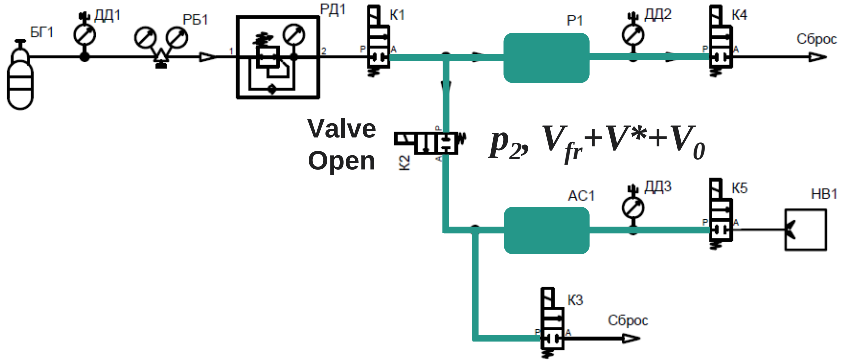
The law of conservation of the amount of matter under the assumption of gas adsorption:

$$\nu_0 + \nu_1 = \nu_2 + \nu_{ads} \quad (6)$$

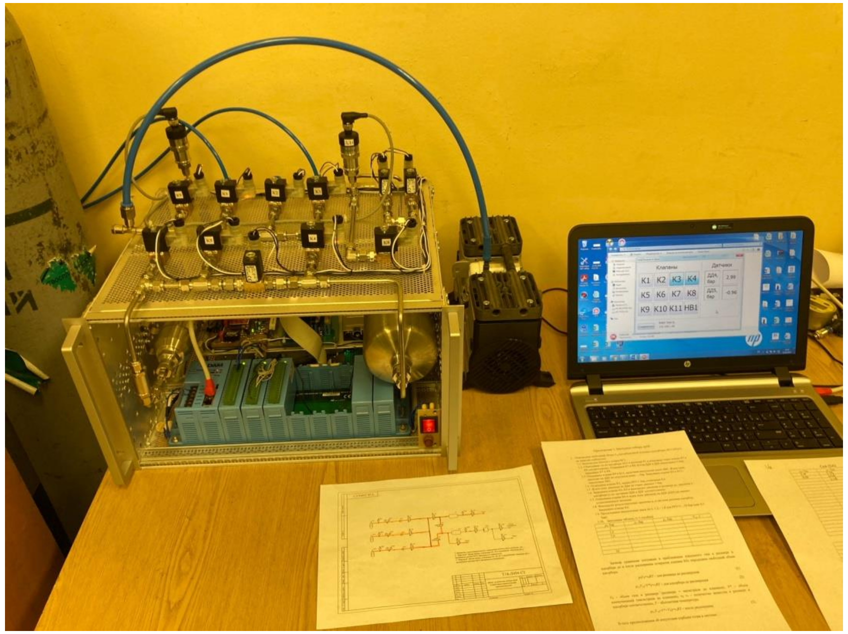
Taking into account (1) – (3):

$$\nu_{ads} = \frac{p_0 V_0 + p_1 (V_{fr} + V^*) - p_2 (V_{fr} + V^* + V_0)}{RT} \quad (7)$$





Results: Setup for investigation of the sorption and separation characteristics of materials



Setup for investigation of the sorption and separation characteristics of materials

Characteristics of the studied sorbents

Sorbent	Manufacturer / Country	Bulk density, kg/l	Real density, kg/l
CaA (5A)	Hong Kong chemical corp.	0,738	1,702
PSA/VPSA (13XHP)	Hong Kong chemical corp.	0,658	1,538
NaX (13X)	Silkem	0,607	1,525
ZSM-5	China	0,600	1,559
Ag-ZSM-5	Riogen, USA	0,755	1,799
Coconut charcoal	Sri Lanka	0,453	1,273
Activated charcoal (SKT-3)	Russia	0,470	1,269

The setup is intended for gas sampling and investigation of argon (nitrogen, oxygen) adsorption processes in pure form or in mixtures with helium on various sorbents at pressures from 0 to 10 bar and at room temperature. The setup allows studying various sorption materials, as well as obtaining adsorption isotherms of gases. The setup also allows determining the real density of porous materials.

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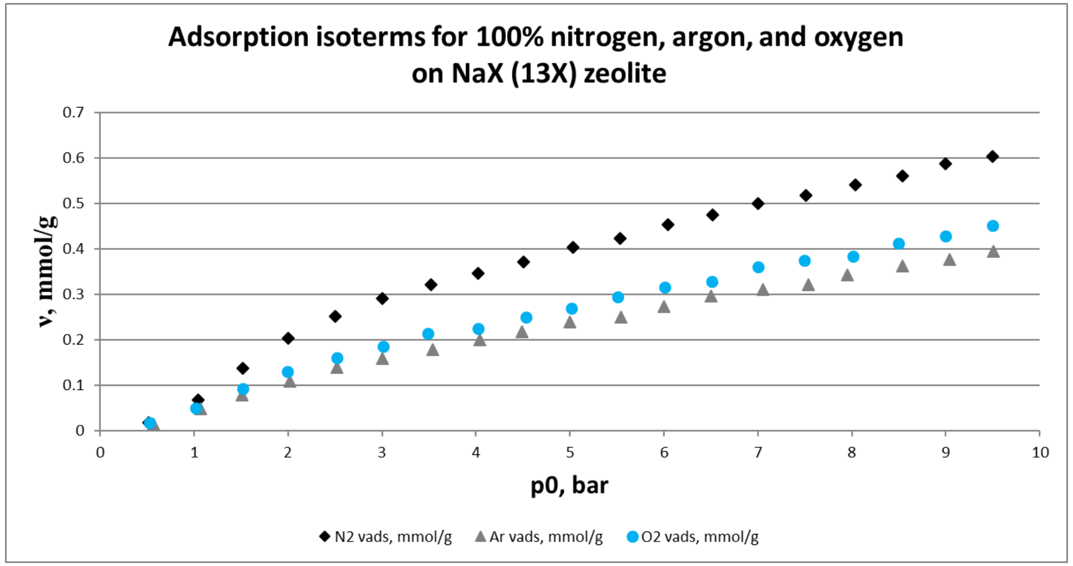
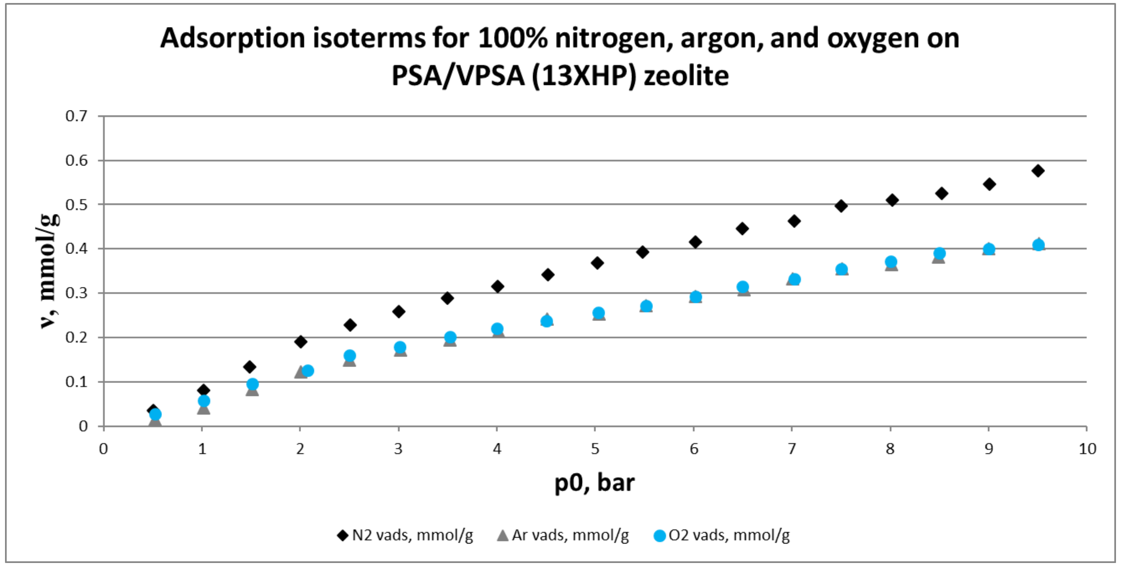
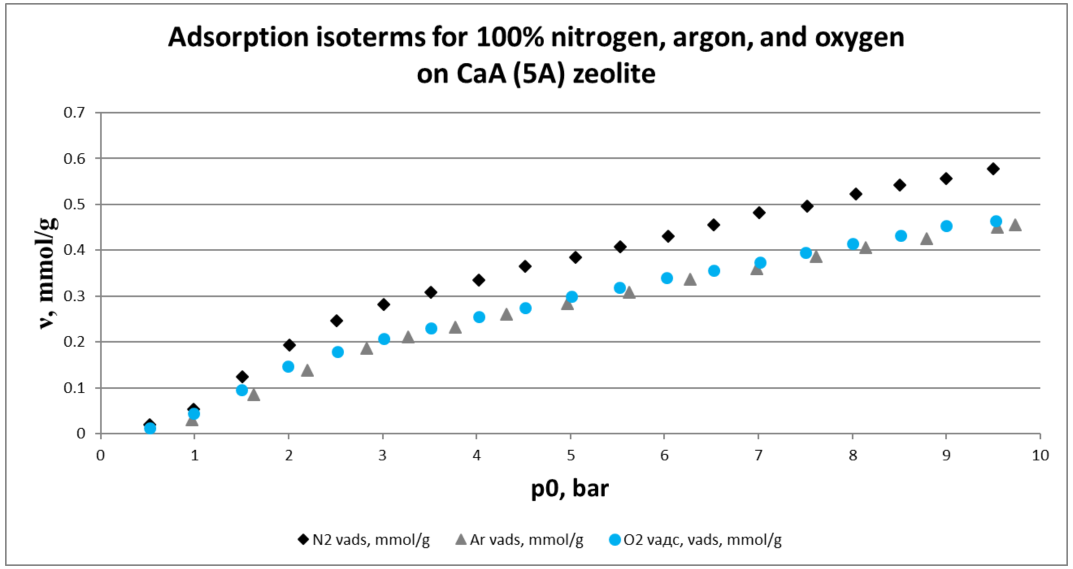
Results: Adsorption isotherms







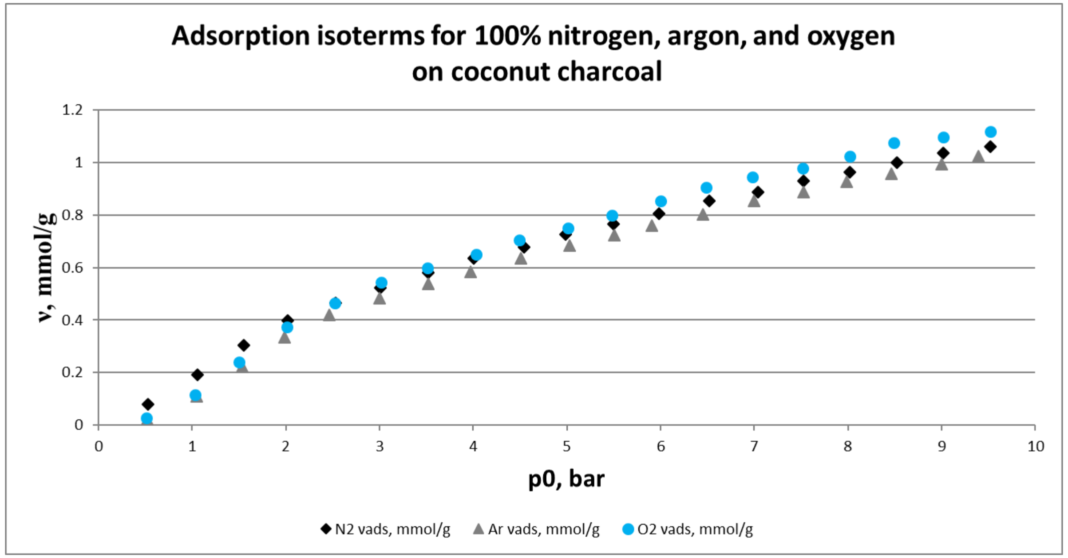
It can be seen that the adsorption isotherms are almost linear at pressures of up to 2.5-3.0 bar. In this range, isotherms can be described by the Henry equation:

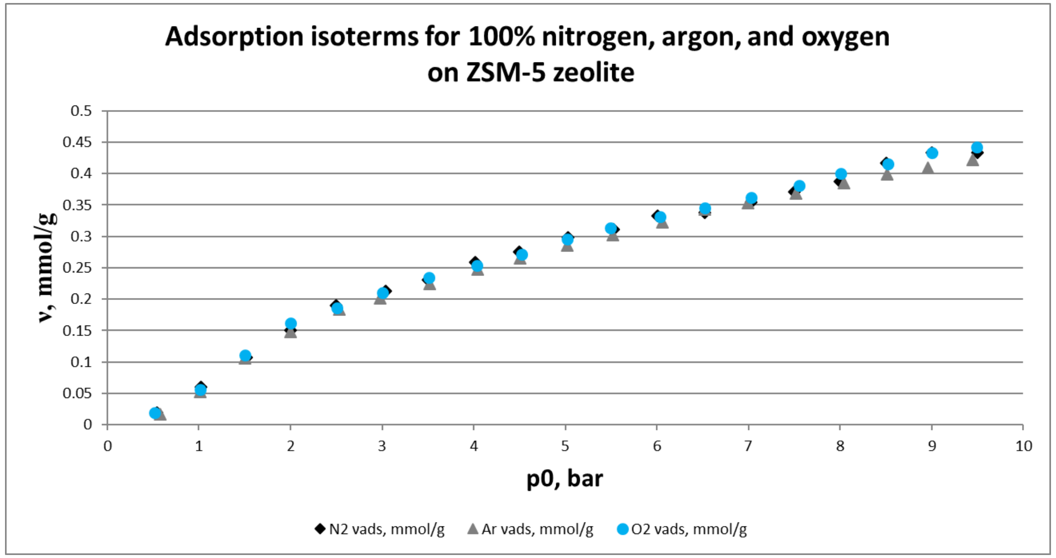
$$v = Kp_0 \quad (8)$$

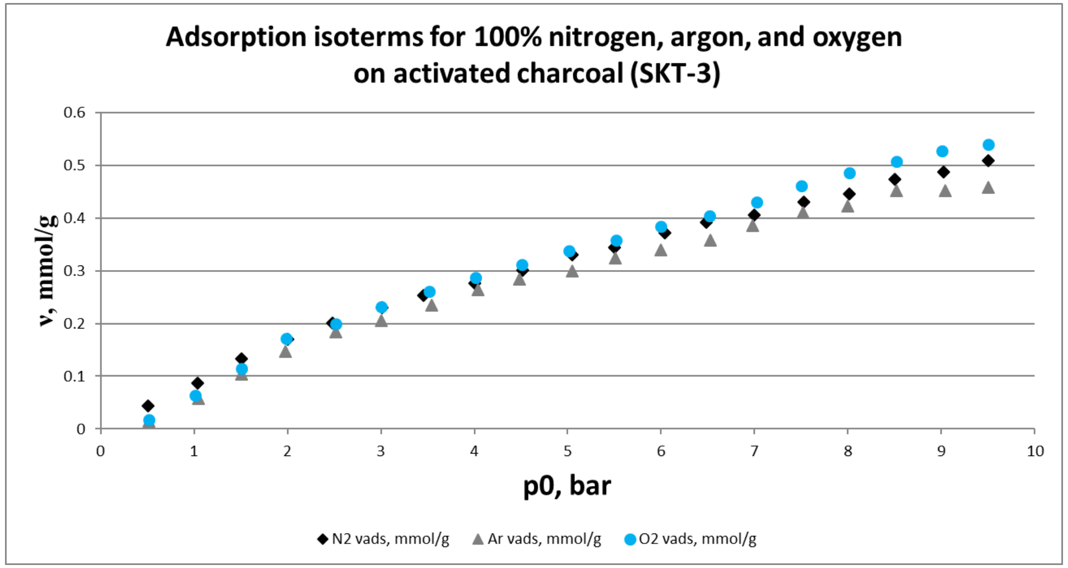
where K is Henry's constant.

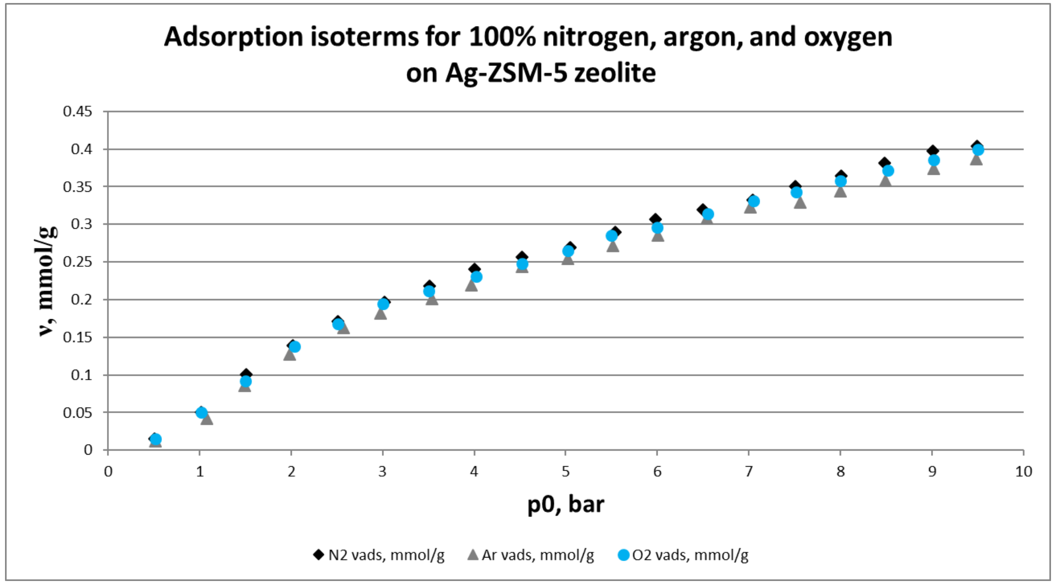
- NaX (13X), CaA (5A) and PSA/VPSA (13XHP) zeolites have high nitrogen selectivity.
- The separation coefficients of the N_2-Ar mixture (at 5.0 bar) for NaX (13X) zeolite are 1.24 times higher than for CaA (5A) zeolite and 1.16 times higher than for PSA/VPSA (13XHP).
- The separation coefficients of the N_2-O_2 mixture (at 5.0 bar) for the NaX (13X) zeolite are 1.16 times higher than for the CaA (5A) zeolite and practically coincide with PSA / VPSA (13XHP).

Results: Adsorption isotherms









Results: Two-stage PSA system for obtaining enriched argon

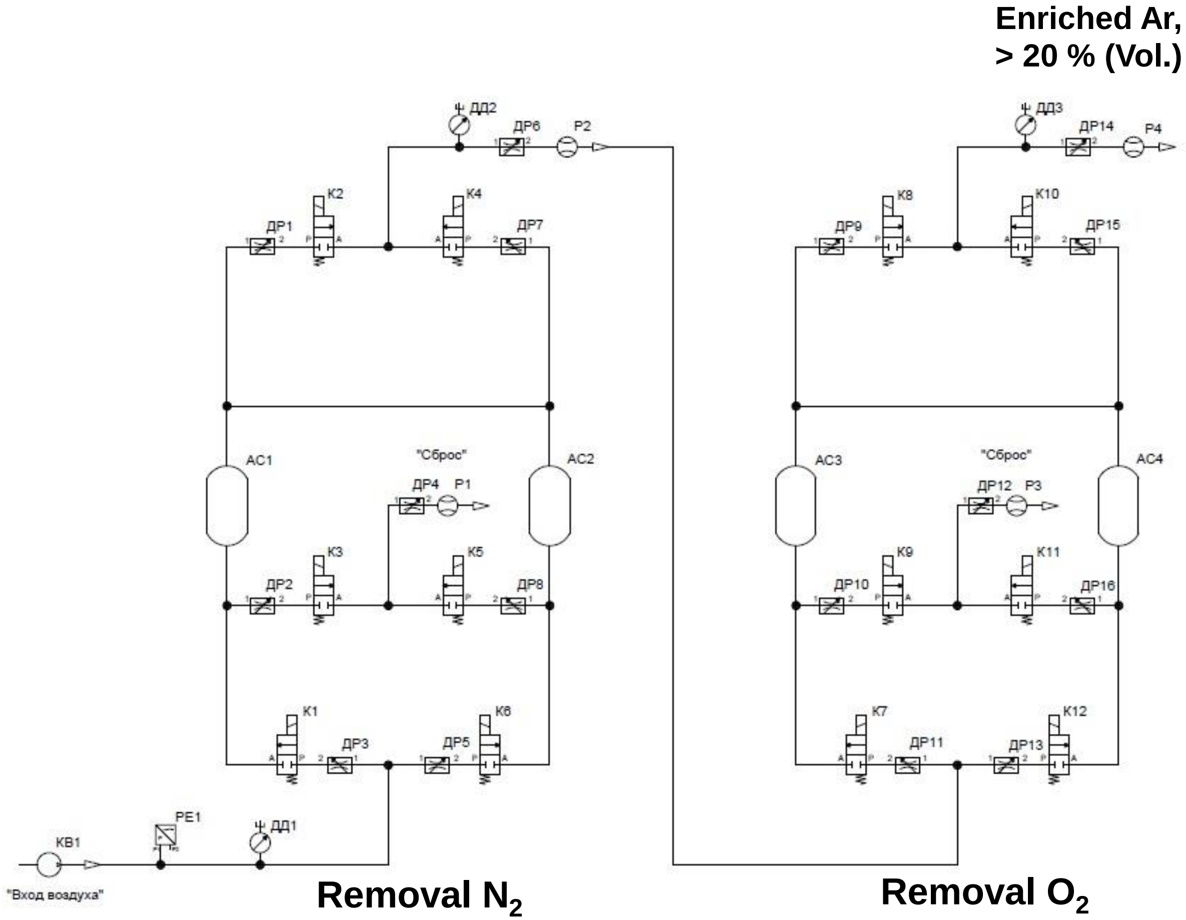
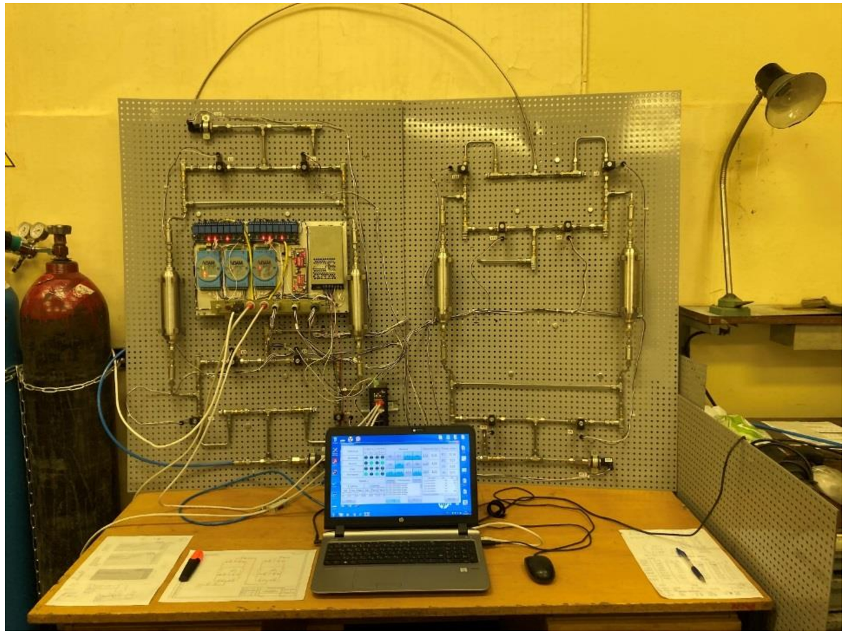


Diagram of the two-stage PSA system for obtaining enriched argon (the Scarstrom variant)



Two-stage PSA system for obtaining enriched argon

The first stage adsorbers are filled with NaX (13X) zeolite, the second stage adsorbers are filled with coconut charcoal.

After the sampling unit, the argon-enriched mixture is sent to the processing (purification) unit. In this unit, enriched argon is purified of nitrogen and oxygen, as well as of other noble gases (Kr, Xe, Rn) using the preparative gas chromatography method.

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Conclusion

1. A setup has been developed for investigation of the sorption and separation characteristics of materials for argon extraction and processing.

2. The sorption and separation characteristics of materials for air separation and argon extraction from an air sample in the pressure range from 0 to 10 bar at room temperature have been studied.

3. A two-stage PSA system has been developed for obtaining enriched argon.

At the next stage of the work, we plan to study the dependence of the argon concentration in an enriched flow on the filling, blowing, discharge, and regeneration times, sorbent types, and adsorbers volumes.

References

1. Liang Na, Discrimination of non-radiation backgrounds in the proportional counter of MARDS, Nuclear Instruments and Methods in Physics Research A, 2017, v. 848, pp. 99–105. https://doi.org/10.1016/j.nima.2016.12.052

2. Ivashkin N.V. Study of the background and yields of 133Xe and 37Ar during camouflage UNEs / N.V. Ivashkin. - Snezhinsk: RFNC Publishing House - VNIITF, 2002. - 21 p.

3. Riedmann R.A., Purtschert R. Natural ^{37}Ar Concentrations in Soil Air: Implications for Monitoring Underground Nuclear Explosions// Environmental Science & Technology. – 2011. – 45(20). – p. 8656-8664.https://doi.org/10.1021/es201192u

4. Grupen C. et al. Particle detectors. – Cambridge: Cambridge university press, 2008. – T. 10.

5. Epifanova V.I., Axelrod L.S. (ed.). Air separation by deep cooling: Technology and equipment: In 2 volumes - 1973.

6. Riedmann R.A., Purtschert R. Separation of argon from environmental samples for Ar-37 and Ar-39 analyses// Separation and Purification Technology. – 2016. – 170. – p. 217-223. https://doi.org/10.1016/j.seppur.2016.06.017

7. J.O. Hirschfelder, Ch.F. Curtiss, and R.B. Bird. Molecular Theory of Gases and Liquids. New York, Wiley; London, Chapman and Hall, 1954.