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INTEGRATED ADSORPTION AND CRYOGENIC DISTILLATION SYSTEM FOR THE RECOVERY AND PURIFICATION OF KRYPTON AND XENON: AN INDUSTRIAL CASE STUDY

Summary. *A descriptive industrial case study of an adsorption and cryogenic distillation complex used to recover and purify krypton and xenon from spent gas mixtures is presented here, drawing on the author's professional experience together with non-public technical and operating documents and published studies of cryogenic distillation, adsorption, process automation, and noble-gas recovery. Its scope spans catalytic oxidation of hydrogen and hydrocarbons, cyclic adsorption of water and carbon dioxide, cryogenic distillation in krypton and xenon columns, automated control of oxygen dosing, pressure, temperature, and refrigerant flow, and gravimetric monitoring during cylinder filling. Krypton and xenon purities of up to 99.9998 percent, target-gas losses below 3 percent during routine operation, and recovered gas equivalent to 15 to 30 percent of consumption are reported for the examined facility, though independent verification is required. Based on this evidence, the case identifies the operating relationships among the process units and the conditions required to return purified krypton and xenon to industrial use.*

Key words: *cryogenic distillation, adsorption purification, krypton recovery, xenon recovery, process automation, noble-gas recycling.*

Introduction. Advances in microelectronics, laser technology, medical equipment, and aerospace engineering have increased industrial demand for rare noble gases, particularly krypton and xenon [7; 8]. Glueckauf and Kitt reported atmospheric concentrations of 1.14 parts per million for krypton and 0.087 parts per million for xenon in 1956 using low-temperature gas chromatography with a radioactive tracer [11]. These early measurements illustrate the scarcity of both gases in air. Large-scale air separation units are therefore required for their commercially viable recovery [8]. Only a limited number of facilities worldwide can produce krypton and xenon at the purity levels required by the electronics and medical industries. Ukraine has historically been an important supplier of purified noble gases [8].

Russia's full-scale invasion of Ukraine in February 2022 exposed the vulnerability of this supply structure: the European Commission's Joint Research Centre reports that Russia and Ukraine together supplied approximately 47 percent of the European Union's rare-gas imports in 2021 [8]. Ukrainian production disruptions contributed to price increases and intensified concerns about the availability of neon, krypton, and xenon, with the JRC reporting xenon and krypton price rises of approximately 50 percent during the first months of the invasion and an even greater increase for neon [8]. Industry reports also documented production disruptions and the need for semiconductor and laser-equipment manufacturers to diversify their supply chains [9; 10]. Together, these pressures increased interest in technologies that reduce noble-gas losses and allow spent gases to be recovered and reused.

Industrial recovery of krypton and xenon from air is based primarily on cryogenic air separation, in which liquefied air is separated into its components according to differences in boiling points [7].

Published literature provides limited information on the coordinated use of these methods in a continuous industrial krypton and xenon recovery complex. The aim of this study is to describe the integrated operation of Psatii's complex and to compare its functional units with the corresponding approaches reported in the literature.

Literature review. Cryogenic distillation remains the principal industrial method for air separation and noble-gas recovery. Zhi et al. examined how the corrugation angle, height, and width of structured packing influence flow and mass-transfer performance in systems containing liquid nitrogen and oxygen [1]. Their results showed that packing geometry affects both separation efficiency and pressure drop, confirming the need to balance mass-transfer performance against hydraulic resistance. Because these experiments were limited to nitrogen and oxygen, applying the reported relationships to krypton and xenon concentrates requires additional validation.

Gas-hydrate separation has been investigated as an alternative to conventional cryogenic distillation. Matizakurima et al. increased the xenon concentration from 25.7 to 80.4 percent after two hydrate formation and dissociation stages and reported an estimated energy cost advantage of approximately 20 percent compared with cryogenic distillation [2]. Chu and Shin likewise demonstrated selective xenon capture from xenon-krypton mixtures using clathrate hydrates [3]. Both studies were conducted with model mixtures under laboratory conditions.

Adsorption research has focused particularly on metal-organic frameworks, commonly referred to as MOFs. Zhou et al. reviewed MOF structures and adsorption mechanisms used for xenon and krypton separation [4]. Choi et al. developed and simulated a two-stage, four-bed vacuum pressure swing adsorption process using experimentally measured adsorption data for a model semiconductor waste-gas stream containing 0.1 mol% xenon in nitrogen [5].

Limited to a model feed stream, the simulation produced xenon at 99.9 percent purity.

Santos et al. developed a fuzzy gain-scheduling strategy for PID control of a cryogenic process [6], addressing temperature control in a single cryogenic unit. By contrast, the present case requires simultaneous control of adsorption regeneration, column pressure control, condenser cooling, and reactant dosing, representing a separate engineering task.

Staicu et al. reviewed heat transfer, insulation, evaporation losses, and safety requirements for cryogenic storage systems [7]. The authors reported that optimized multilayer insulation can reduce radiative heat loads by approximately 40 to 60 percent. Their review centers on large cryogenic tanks, leaving the handling and quality control of small batches unaddressed.

Concentration of noble-gas production in a limited number of countries was identified by the European Commission's Joint Research Centre as a supply-security risk [8], with industry publications further describing the effects of production shutdowns in Ukraine on semiconductor and laser-equipment supply chains [9; 10]. Together, these reports connect noble-gas recovery with supply security, addressing disruption and market effects without examining the technical configuration of individual recycling facilities.

Materials and methods. Psatii Anatolii's engineering work during his employment at the Research and Engineering Center of a specialized noble-gas producer in Odesa, Ukraine, concerning the purification, separation, recovery, and reuse of krypton, xenon, neon, and helium, is the subject of this study. Internal technical documentation, organizational records, letters from project participants, and implementation materials relating to the industrial complex form the basis of the case description; these non-public materials, described here as supporting materials, are omitted from the reference list.

A descriptive industrial case-study design underlies this analysis, in which supporting materials were reviewed to identify the functional units of the

complex, operating ranges, control logic, and reported performance indicators. Information was organized by process stage, including preliminary purification, adsorption, cryogenic distillation, automated control, and cylinder filling, and compared with the published research cited in the literature review. Because the analysis is limited to the reviewed case materials, the results apply to the examined facility, and wider industry applicability requires separate measurements and external validation.

Results. *Preliminary Purification of the Mixture*

Feedstock processed by the complex consists of residual krypton and xenon mixed with nitrogen, argon, oxygen, hydrogen, water vapor, carbon dioxide, and hydrocarbons, generated by manufacturing processes in the medical, lighting, electronics, and laser industries. Hydrogen and hydrocarbon impurities are removed by catalytic oxidation at 690 to 720 K (417 to 447 °C), which converts hydrogen to water and hydrocarbons primarily to carbon dioxide and water. Cold traps and adsorbers subsequently remove these reaction products; the operating temperature must remain sufficient to sustain the reaction yet low enough to prevent reactor instability. Excessive oxygen dosing can create an unsafe hydrogen-oxygen ratio and increase the risk of oxidation of carbonaceous adsorbents. Psatii developed an automatic dosing system that adjusts the oxygen supply according to the gas flow rate and measured hydrogen concentration over the reported range of 0 to 5.5 percent hydrogen.

Two adsorbers operate alternately. One removes water and carbon dioxide from the gas mixture, and the other undergoes regeneration with hot nitrogen at 120 to 130 °C (393 to 403 K). The adsorption cycle lasts approximately one week. Regeneration takes about half that time. Alternating between two adsorbers in this way supports continuous operation, with nitrogen from the refrigeration stage reused as the regeneration gas to reduce additional consumption.

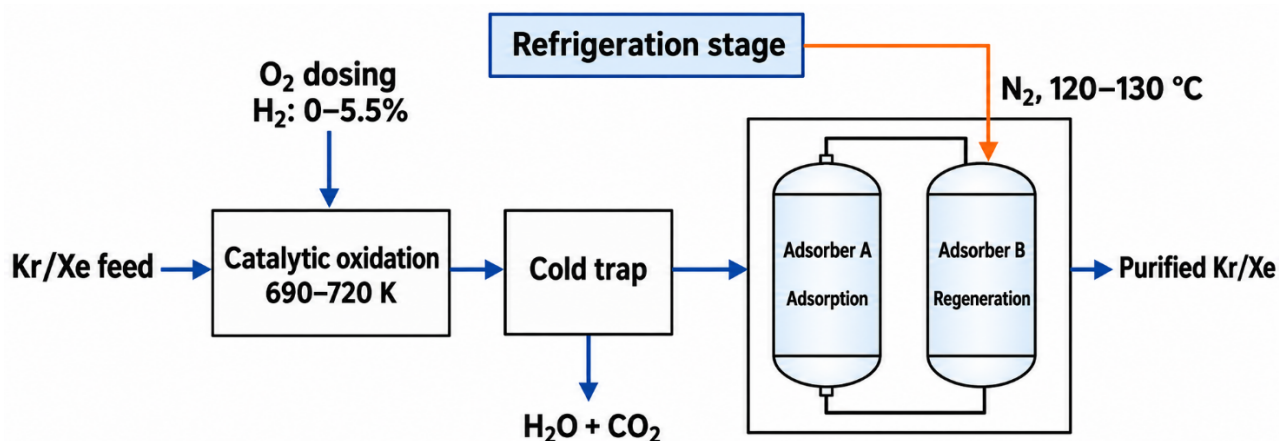


Fig. 1. Process Flow Diagram for Preliminary Purification of a Krypton and Xenon Gas Mixture

Cryogenic Distillation and Automated Control

Two cryogenic distillation columns make up the xenon purification line: the first operates at -110 to -50 °C (163 to 223 K) and removes residual heavy hydrocarbon impurities, while the second operates at 120 to 180 K (-153 to -93 °C) and separates xenon from more volatile components, including nitrogen and argon. High-purity xenon accumulates in the column sump and is subsequently transferred to cylinders. Comparative tests assessed three packing types in terms of separation efficiency and hydraulic resistance. Spiral-prismatic packing provided slightly higher separation efficiency and produced a greater pressure drop. Mesh packing produced a lower pressure drop and lower mass-transfer performance. Under the documented operating conditions, spiral-cylindrical packing provided the most suitable balance between these criteria.

Using the same criteria as the xenon distillation system, the krypton distillation column was evaluated through tests with 8×8 mm spiral-cylindrical packing, with a reported specific surface area of $1100 \text{ m}^2/\text{m}^3$, to assess separation efficiency and pressure drop. Product purity for the resulting pilot-production batches of krypton and xenon, using this configuration, was verified by gas chromatography.

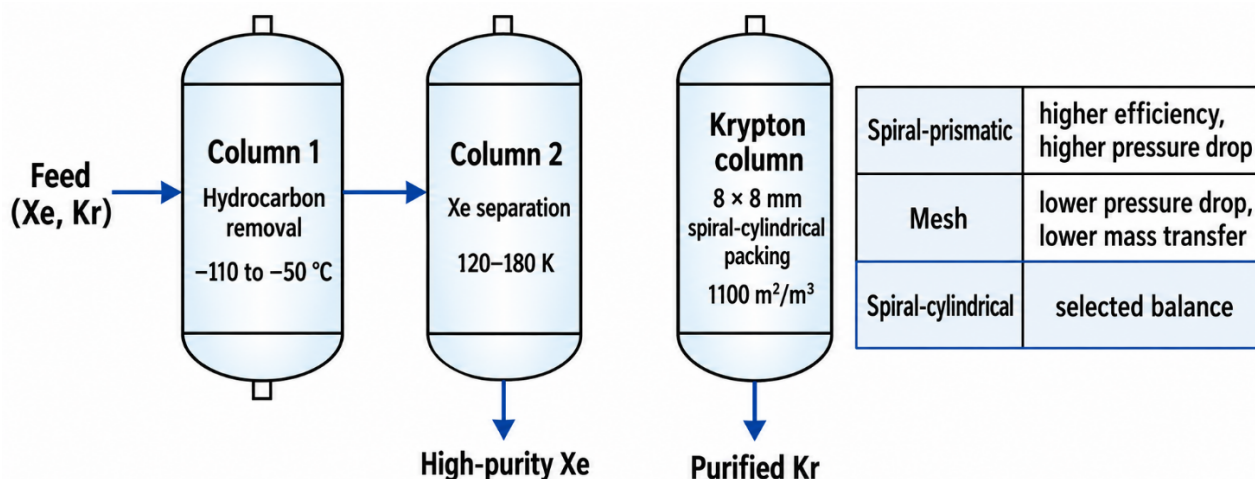


Fig. 2. Cryogenic Distillation System and Packing Selection for Krypton and Xenon Purification

For the liquid-nitrogen-cooled condensers, Psatii proposed additional sealed sections with an increased heat-transfer area. Krypton served as the intermediate heat-transfer gas in the sealed section of the first column. Argon served the same function in the second column. Changing the pressure of the intermediate gas altered the effective heat transfer between the refrigerant and the column. Gradual adjustment of the cooling rate in this way reduced the risk of abrupt temperature changes and component freezing, with the selected combination of gas type, pressure, and refrigerant flow supporting stable column operation within the documented operating range.

The automation system maintains pressure, temperature, refrigerant flow, column operating modes, and adsorber regeneration cycles with limited operator intervention. Remote monitoring and authorized adjustment of control parameters are available through the plant control network. Column pressure is controlled by a PID loop. Separate tuning parameters were used for the pressure and condenser-temperature loops to account for their different dynamic responses and to limit overshoot.

Product Filling and Quality Control

Filling the finished product into cylinders and quality control are handled by the final unit of the complex. Each cylinder is weighed to determine the mass of the product. Automatic valves connect the cylinders to the compressor outlet, the consumer supply line, the gas-analysis line, or the recovery tank. Under normal operating conditions, the first cylinder supplies xenon to the consumer through a pressure regulator that reduces the pressure from 70 to 5.5 bar. Purified xenon from the sump of the second column fills the second cylinder, which can be connected to a gas chromatograph for purity analysis, while the third remains available for reserve or emergency recirculation. Psatii selected this three-position arrangement because it allows product supply, cylinder filling, and quality analysis to proceed without interrupting one another.

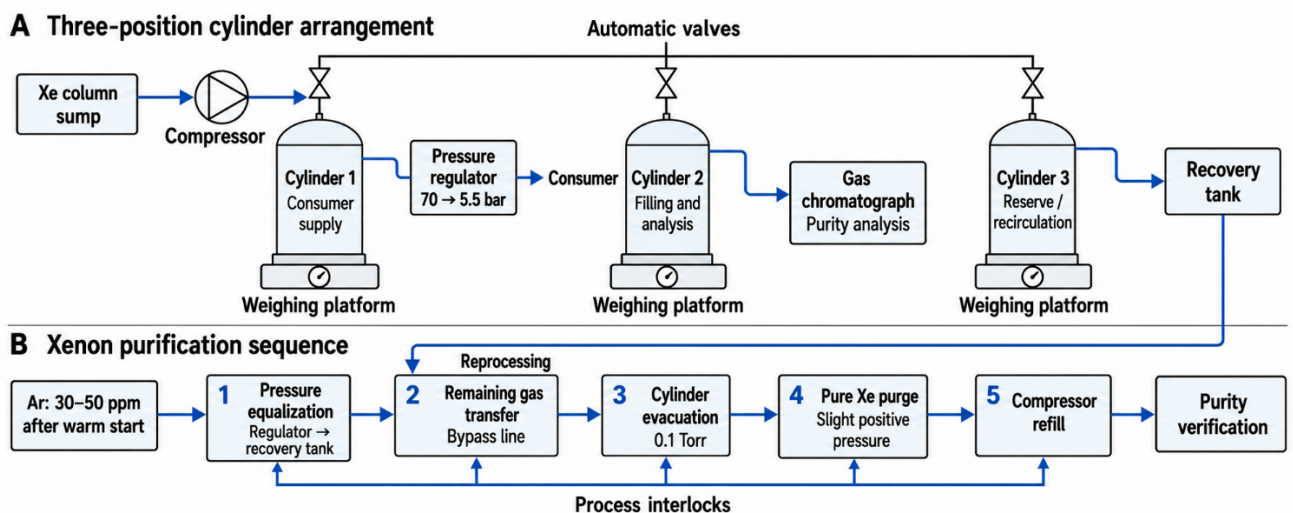


Fig. 3. Product Filling, Quality Control, and Xenon Repurification System

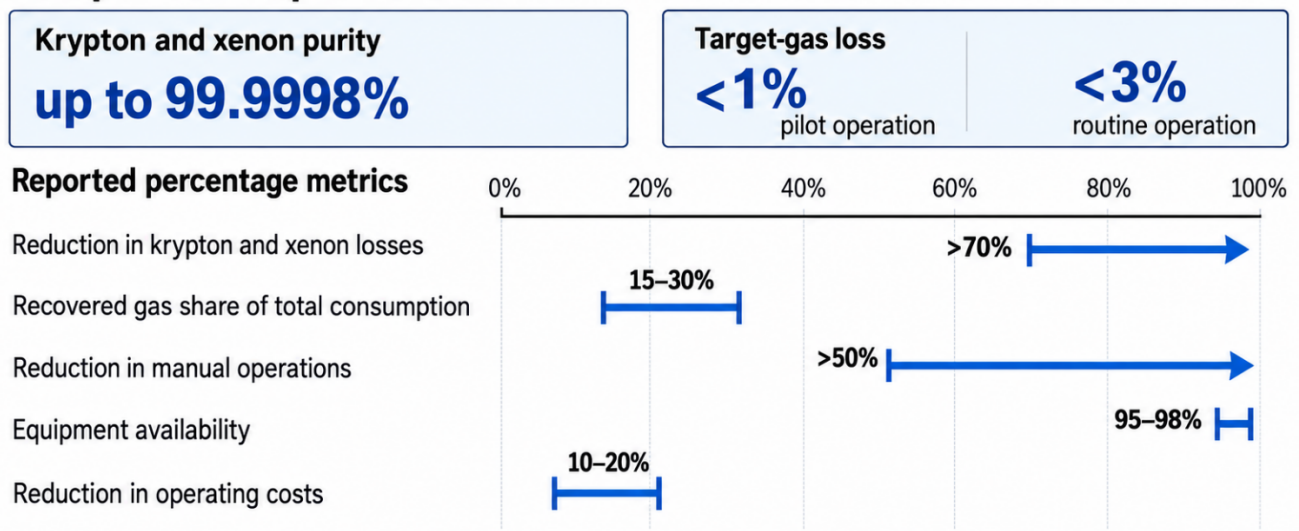
After a warm start, residual argon may reach 30 to 50 parts per million because of stagnant gas remaining in the pipelines. When this occurs, the cylinder undergoes a repurification procedure. Repurification begins with the gas transferred through the pressure regulator to the recovery tank until the pressure equalizes, after which the remaining gas is routed through the bypass line. After atmospheric pressure is reached, the cylinder is evacuated to 0.1 Torr, isolated from the vacuum line, purged with pure xenon to a slight positive pressure, and refilled through the compressor. Process interlocks prevent the next stage from

starting until the preceding stage has been completed. Together, these steps minimize contact with air and allow the gas batch to be reprocessed instead of discarded.

Industrial Performance Metrics

Reviewed case materials report krypton and xenon purities of up to 99.9998 percent, target-gas losses below 1 percent during pilot operation and below 3 percent during routine operation, a reduction of more than 70 percent in krypton and xenon losses, recovered gas equivalent to 15 to 30 percent of total consumption, a reduction of more than 50 percent in manual operations, equipment availability of 95 to 98 percent, and a 10 to 20 percent reduction in operating costs, though these values were not independently verified for this study. Payback period estimates range from two to four years, with indicative annual savings of approximately \$400,000 for a medium-capacity unit and \$1 million to \$2 million for a large industrial complex.

A Operational performance



B Indicative techno-economic assessment



Reported in the reviewed case materials; values were not independently verified for this study.

Fig. 4. Reported Industrial Performance and Indicative Techno-Economic Metrics for the Krypton and Xenon Recovery Complex

Discussion of results. Catalytic purification, cyclic adsorption, cryogenic distillation, process automation, and product quality control are documented here as a coordinated operation within one industrial noble-gas recovery system; the engineering contribution concerns the interaction of these operations in a continuous recovery process.

Zhi et al. examined structured packing in nitrogen and oxygen systems and demonstrated the influence of packing geometry on mass-transfer performance and pressure drop [1]; the industrial tests described in this case applied the same general selection criteria to the purification of rare-gas mixtures, though differences in feed composition and operating conditions prevent direct quantitative comparison with their results. A comparable qualitative relationship between separation efficiency and hydraulic resistance was nonetheless documented.

Hydrate-based separation and MOF-based adsorption directly target xenon and krypton separation [2; 3; 4; 5], whereas the adsorption stage in the complex examined here performs a different function, removing water and carbon dioxide ahead of cryogenic distillation. Both may be complementary at the process level, though their regeneration mechanisms differ: Choi et al.'s VPSA process relies on pressure and vacuum cycling [5], while the adsorbers examined here are regenerated with heated nitrogen.

Santos et al. investigated fuzzy gain scheduling for the control of a single cryogenic process [6], whereas the system described in this case requires simultaneous control of adsorber regeneration, column pressure, condenser cooling, and oxygen dosing. Coordination among these loops is necessary because disturbances in one part of the process can affect the operation of the other units.

Staicu et al. focused primarily on the storage and transportation of liquefied gases in large cryogenic tanks [7], whereas this case concerns the handling, analysis, and repurification of high-purity product in compressed-gas cylinders.

Including chromatographic analysis and repurification links cylinder management to the gas-recovery process.

Recovery rates reported for the complex are also relevant to the supply-security concerns identified by the European Commission's Joint Research Centre [8], since reusing 15 to 30 percent of total gas consumption can reduce the need to purchase primary krypton and xenon. Because the reported values apply to one facility, validation at additional plants is required before broader use.

Several limitations apply to this study. Because the performance indicators were taken from non-public supporting materials, a separate experimental program was outside its scope. Since the reported purity, loss, availability, and economic indicators concern only one facility and may vary with plant capacity, feed composition, operating mode, and gas prices, further studies should apply standardized measurement and reporting procedures across several industrial facilities.

Conclusions. Catalytic oxidation of hydrogen and hydrocarbon impurities, cyclic adsorption of water and carbon dioxide, cryogenic distillation, automated process control, and gravimetric monitoring during cylinder filling together form the continuous noble-gas recovery system analyzed in this case study. Coordinated application of these established operations allows spent industrial gas mixtures to be purified and returned to use.

Reported product purity, recovery of part of the consumed gas, and reduced target-gas losses are high for the examined facility, though independent validation is required before broader use. Application at other facilities would require adjustment to feed composition, plant capacity, and product specifications.

Author's contribution. Five engineering solutions are attributed to Psatii Anatolii by the supporting materials:

- coordinated cyclic operation of two adsorbers and reuse of nitrogen for regeneration;

- automatic oxygen dosing based on the gas flow rate and hydrogen concentration;
- pressure-controlled condenser sections for gradual adjustment of cooling;
- gravimetric monitoring and three-position cylinder management; and
- a procedure for recovering and reprocessing off-specification gas from a cylinder.

Examined here, the engineering contribution is the integration of established operations within a single continuous process.

Prospects for further research. Future research should evaluate the system at different production capacities, quantify its performance across a wider range of feed compositions, and compare the results using standardized purity and loss metrics. Hybrid configurations combining cryogenic distillation with MOF-based adsorption or hydrate separation also warrant investigation. A separate techno-economic analysis should examine the sensitivity of recovery costs to gas prices, energy consumption, plant capacity, and the proportion of gas returned to circulation.

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