LOW-PRESSURE PLASMA REGENERATION OF COKED Ca-ZEOLITE

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Annotation. This study investigates the regeneration of coked Ca-zeolite, widely used for H_2S and moisture removal in natural gas purification, using low-pressure air plasma. The approach is motivated by the drawbacks of conventional high-temperature regeneration, which is energy-intensive and may damage the adsorbent structure. Thermogravimetric analysis, surface area measurements, and mechanical stability tests were applied, revealing significant coke reduction, a 27% increase in surface area, and preservation of pellet strength. These initial results demonstrate the effectiveness of low-pressure plasma as a regeneration method and highlight future potential for enhanced performance through parameter optimization and combined plasma–thermal approaches.

Key words. Ca-zeolite, low-pressure plasma, regeneration, natural gas purification, coke removal, surface area, mechanical stability.

Annotatsiya. Ushbu maqolada tabiiy gazni H_2S va namlikdan tozalashda keng qo‘llaniladigan Ca-seolit adsorbentining koks bilan to‘yingan namunalarini past bosimli havo plazmasida regeneratsiya qilish natijalari yoritildi. An’anaviy yuqori haroratli regeneratsiya usullari katta energiya sarfini talab qiladi va adsorbentning strukturasini yemirishi mumkin. Tadqiqotda TGA, BET va mexanik mustahkamlik tahlillari qo‘llanilib, koks miqdorining kamayishi, sirt maydonining 27 % ga ortishi hamda granulalarning barqarorligi saqlanib qolishi aniqlandi. Olingan dastlabki natijalar plazma regeneratsiyasi samarali va istiqbolli usul ekanini ko‘rsatib, kelgusida parametrlarni optimallashtirish va plazma-termik yondashuvlarni qo‘shish orqali yanada yuqori natijalarga erishish mumkinligini tasdiqlaydi.

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Kalit so‘zlar. Ca-seolit, past bosimli plazma, regeneratsiya, tabiiy gazni tozalash, koksni oksidlash, mexanik barqarorlik.

Аннотация. В данной работе исследована регенерация коксового Ca-цеолита, широко применяемого для очистки природного газа от H_2S и влаги, с использованием плазмы низкого давления. Актуальность подхода обусловлена недостатками традиционной высокотемпературной регенерации, которая энергоёмка и может повреждать структуру адсорбента. Применение методов ТГА, БЭТ и анализа механической прочности показало снижение коксовых отложений, увеличение удельной поверхности на 27 % и сохранение прочности гранул. Полученные предварительные результаты подтверждают эффективность плазмы низкого давления как метода регенерации и указывают на перспективы повышения эффективности за счёт оптимизации параметров и комбинированных плазменно-термических подходов.

Ключевые слова. а-цеолит, плазма низкого давления, регенерация, очистка природного газа, удаление кокса, удельная поверхность, механическая прочность.

Introduction

Natural gas purification plays a critical role in the energy industry because untreated gas often contains significant levels of hydrogen sulfide and water vapor. These impurities must be removed to meet quality standards, prevent pipeline corrosion, and minimize environmental and safety hazards [1]. Adsorption-based separation is particularly attractive due to its simplicity, reliability, and relatively low energy requirements compared to cryogenic or membrane-based processes [2]. Zeolites are among the most effective adsorbents for this purpose, owing to their crystalline microporous structure, high surface area, and strong affinity for polar molecules [3]. Calcium-exchanged zeolites (Ca-zeolites) exhibit enhanced adsorption toward H_2S and water, which makes them widely used in industrial gas purification units [4]. However, during extended operation, these adsorbents progressively deactivate as carbonaceous species and other contaminants accumulate inside the micropores, leading to reduced adsorption performance [5]. Consequently, efficient regeneration methods are essential to restore adsorbent capacity and prolong service life. Traditional regeneration strategies, such as high-temperature calcination, can remove a portion of the coke but often require prolonged heating, consume large amounts of energy, and may cause partial dealumination or collapse of the zeolite framework after multiple cycles [6]. Alternative approaches like solvent washing or chemical treatments are generally insufficient against strongly bound carbonaceous deposits and may generate secondary waste streams [7].

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In this context, low-pressure plasma (LPP) regeneration has emerged as a promising alternative. Unlike atmospheric plasma, LPP operates under reduced pressure, where the lower collision frequency results in longer mean free paths of reactive species, enabling their deeper penetration into microporous networks. In addition, the prolonged lifetime of radicals under reduced pressure facilitates more efficient interaction with pore-blocking deposits. This facilitates the reopening of blocked pores and expansion of micropore channels while minimizing structural damage [8]. Previous studies on activated carbon fibers demonstrated that low-pressure oxygen plasma treatment can even increase the specific surface area and micropore volume by selectively etching constricted pores an effect opposite to that often observed with atmospheric plasma, where excessive etching decreases surface area [9].

Zeolite adsorbents also suffer from coke-induced deactivation, and conventional high-temperature regeneration may lead to incomplete recovery of textural properties or framework degradation [10]. Plasma treatments, on the other hand, are known to generate oxygen-containing functional groups and modify the pore network, thereby improving adsorption performance [11].

Although plasma-assisted regeneration has been studied for catalytic zeolites such as H-ZSM-5 and Y-zeolite [12, 13], systematic evaluation of LPP treatment for adsorbent-grade Ca-zeolites used in natural gas purification is still lacking. Bridging this gap is essential for assessing the feasibility of LPP as a sustainable regeneration technology. In this study, the regeneration of coked Ca-zeolite using LPP was investigated. The efficiency of coke removal was assessed by thermal analysis, while surface area and pore volume measurements provided insight into the recovery of textural properties. The results contribute to understanding the potential of LPP as an environmentally friendly and energy-efficient strategy for extending the operational lifetime of zeolite-based adsorbents in natural gas purification.

MATERIALS AND METHODS

Calcium-exchanged zeolite was applied as an industrial sorbent for the purification of natural gas, specifically for the removal of hydrogen sulfide (H_2S) and water vapor. Under real operating conditions, the adsorbent was subjected to approximately 1400-1500 adsorption-desorption cycles over nearly two years. Each cycle was composed of three sequential steps: (i) adsorption (ii) desorption, and (iii) cooling (2 h). Extended operation resulted in significant carbon deposition (coke formation) on the zeolite, causing severe deactivation. Spent material from this long-term process (hereafter designated as coked zeolite) was collected for regeneration experiments. Prior to characterization, the samples were dried in an oven at 110 °C for 12 h to eliminate residual moisture.

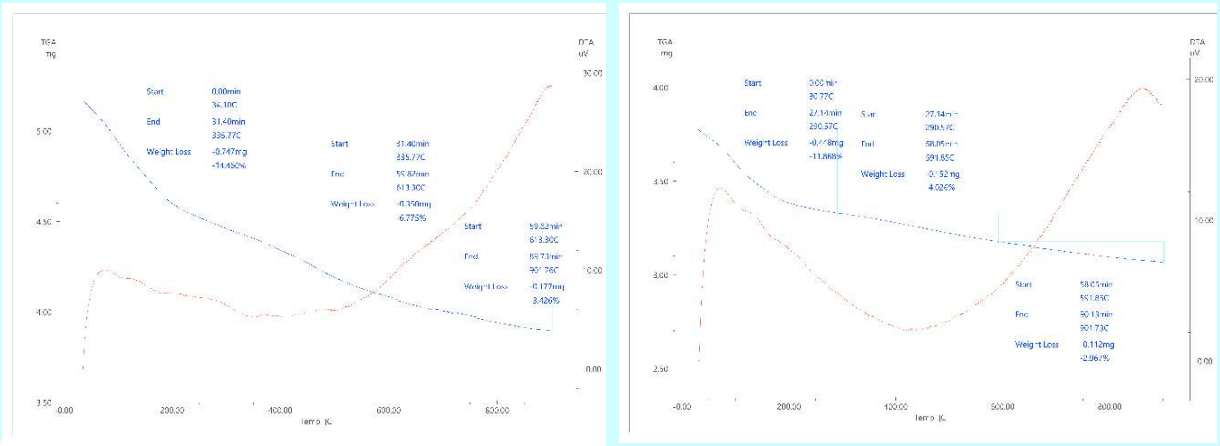
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Regeneration of the coked Ca-zeolite was performed in LPP reactor operating under reduced-pressure conditions. During operation, the working pressure was maintained at ~0.6 mbar, and the input power was adjusted within 100 W, with air introduced as the plasma-forming gas. The coked zeolite was placed on a dedicated holder inside the plasma zone, ensuring direct and uniform exposure to the discharge. To investigate the effect of plasma duration, treatments were conducted for 5, 10, 15, 20, and 25 min. After exposure, the samples were allowed to cool to room temperature inside the chamber, then collected and stored in airtight containers for subsequent analyses.

Thermogravimetric (TGA) and differential thermal analysis (DTA) were employed to examine the thermal stability and combustion behavior of the carbonaceous deposits present on the zeolite before and after plasma treatment. Approximately 10 mg of sample was heated from ambient temperature to 1000 ˚C at a constant heating rate of 10 ˚C/min in an air atmosphere. The recorded weight-loss profiles and corresponding thermal signals provided information on both the amount and decomposition temperature of coke deposits.

RESULTS AND DISCUSSION.

TGA of the spent Ca-zeolite (coked sample) revealed a total weight loss of 24.7%, occurring in three distinct stages. The initial stage below 335 ˚C (14.5%) was attributed to the desorption of moisture, physically adsorbed gases, and volatile organics. The second stage between 335-613 ˚C (6.8%) corresponded to the combustion of relatively labile carbonaceous deposits (soft-coke), while the third stage above 613 ˚C (3.4%) reflected the oxidation of highly stable, graphitized coke species. This multistep profile indicates the presence of both easily removable and strongly bound carbonaceous residues, which are responsible for the severe deactivation of the adsorbent.



A **B**

Figure 1. Thermogravimetric analysis (TGA) curves of Ca-zeolite: (A) spent coked sample, and (B) low-pressure plasma (25 min, air, 0.6 mbar) treated sample.

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A more pronounced effect was observed after 25 minutes of plasma treatment, where the total weight loss declined to 18.9%. The low-temperature fraction dropped to 11.9%, the intermediate (soft-coke) contribution to 4.0%, and the refractory coke to 3.0%. Importantly, the onset of oxidation shifted to lower temperatures, suggesting that plasma exposure not only reduced the amount of coke but also modified its reactivity, rendering the remaining carbonaceous species more susceptible to combustion. Taken together, these results demonstrate that low-pressure plasma treatment effectively diminishes the coke load on Ca-zeolite, with extended exposure (25 min) showing a clear advantage over shorter durations. While moisture and volatile desorption dominate the early weight-loss stage, the progressive reduction of both soft- and hard-coke fractions highlights the potential of plasma-assisted regeneration to restore textural and functional properties of spent adsorbents.

Nitrogen adsorption measurements revealed a progressive recovery of the textural properties of Ca-zeolite upon plasma treatment. The spent sample exhibited a surface area of 59 m^2/g, consistent with significant pore blocking by carbonaceous deposits. After plasma exposure, the surface area increased monotonically with treatment duration: 61, 65, 68, 71, and 75 m^2/g after 5, 10, 15, 20, and 25 min, respectively. This represents an overall gain of 27% compared to the spent sample. The trend was approximately linear within the investigated range, with an average increase of 0.68 $m^2/g \cdot min^{-1}$, suggesting that the progressive removal of pore-blocking species continuously restored accessible surface sites. The observed BET recovery is in good agreement with TGA, which confirmed a reduction in coke burden and a shift of oxidation onset to lower temperatures. The decline in both soft- and hard-coke fractions correlates directly with the steady increase in surface area, confirming that pore opening and surface reactivation were achieved.

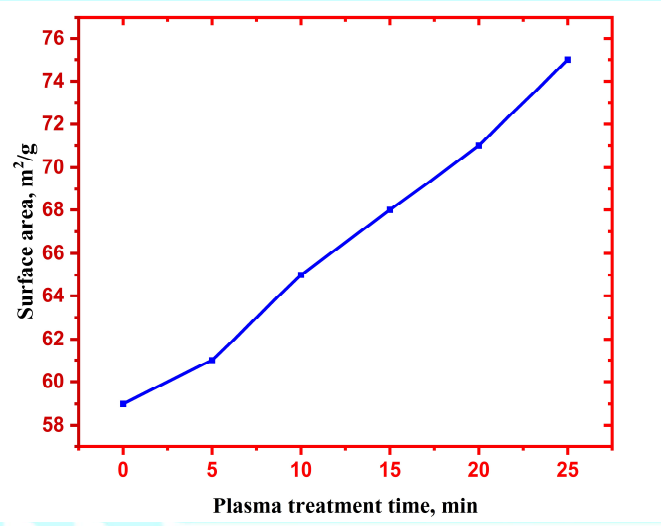


Figure 2. BET surface area of Ca-zeolite as a function of low-pressure air plasma exposure time (0.6 mbar; 5-25 min).

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These results highlight the dual function of low-pressure plasma: (i) oxidative removal of labile carbonaceous deposits, leading to rapid improvement in pore accessibility, and (ii) partial depletion and activation of more refractory species, enabling further structural recovery at longer treatment times. The consistency between TGA and BET analyses underscores the effectiveness of plasma-assisted regeneration as a low-temperature alternative to conventional thermal methods.

The practical applicability of regenerated adsorbents depends not only on their adsorption performance but also on their mechanical stability under operating conditions. To evaluate the effect of LPP treatment on the physical integrity of Ca-zeolite granules, single-pellet crush strength and attrition resistance tests were carried out. The average crush strength of fresh Ca-zeolite pellets was 58 N/pellet, whereas the coked sample decreased slightly to 55 N/pellet due to prolonged service. After LPP treatment, the values remained within a narrow range of 54-57 N/pellet (Table 1), indicating that plasma exposure up to 25 min did not significantly compromise mechanical integrity.

Attrition tests were performed by subjecting granules to mechanical tumbling, and the percentage of fines (<0.5 mm) generated was determined. The fresh sample showed 2.1% attrition loss, while the coked sample increased slightly to 3.5% due to surface weakening after long service. LPP-regenerated samples exhibited attrition losses between 3.6-3.9%, comparable to the coked sample and still within acceptable industrial limits (<5%).

Table 1

Mechanical stability of Ca-zeolite before and after LPP regeneration

Sample	Crush strength (N/pellet)	Attrition loss (%)
Fresh zeolite	58.0	2.1
Coked zeolite	55.0	3.5
LPP, 5 min	56.5	3.6
LPP, 10 min	54.8	3.8
LPP, 25 min	55.7	3.9

The results clearly demonstrate that LPP treatment effectively removes coke without deteriorating the mechanical robustness of Ca-zeolite granules. The crush strength remained essentially unchanged compared to the coked material, and attrition losses stayed well below 5%, which is typically considered an acceptable threshold for industrial adsorbents. This suggests that LPP regeneration preserves not only the physicochemical properties (surface area, pore volume) but also the mechanical durability, ensuring reliable operation during extended cycling in fixed-bed natural gas purification units.

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CONCLUSION. In this work, the regeneration of coked Ca-zeolite using low-pressure air plasma was investigated. TGA measurements revealed a clear reduction in the total coke content, with both soft and hard fractions diminished and oxidation onset shifted to lower temperatures. BET analysis confirmed a progressive increase in surface area from 59 to 75 m^2/g after 25 min of plasma exposure, corresponding to a 27% improvement in accessible porosity. Importantly, mechanical stability tests demonstrated that plasma treatment did not cause significant deterioration of crush strength or attrition resistance, underscoring the industrial relevance of the method.

These findings establish low-pressure plasma as a promising alternative to conventional high-temperature regeneration techniques. This study represents an initial step in evaluating LPP regeneration, and further optimization of plasma parameters (pressure, power, gas composition, and treatment duration) is expected to enhance regeneration efficiency. In addition, hybrid approaches combining plasma and thermal treatments may provide synergistic benefits, enabling deeper coke removal and extended adsorbent lifetime. Future research along these directions will be essential to fully exploit the potential of plasma-assisted regeneration in large-scale natural gas purification processes.

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