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Sodium Cyanide Generation by Coal Gasification

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ABSTRACT

The aim of this study was to evaluate the technological feasibility of producing sodium cyanide through coal gasification. Specifically, it examined the effects of key process parameters—temperature, experiment duration, and coal type—on the concentration of sodium cyanide in the re-sulting solutions, and aimed to identify the optimal operating conditions. Experiments were conducted using a laboratory-scale setup consisting of a tubular cylindrical furnace with a corundum tube as the working compartment. Lignite and charcoal, pre-crushed to increase their specific surface area, were used as feedstocks.

Sodium cyanide was produced by sorbing gaseous hydrogen cyanide (a component of the syngas) into a sodium carbonate solution. An NaOH solution (pH = 10), maintained in an ice bath, was used in the absorber system to stabilize the cyanide. The concentration of sodium cyanide in the final solution was determined using a titrimetric method. The thermodynamic modeling was performed using the HSC Chemistry 5.1 software package. When charcoal was gasified at temperatures between 600 °C and 800 °C, sodium cyanide concentrations in the range of 0.03–0.08 wt.% were obtained. However, increasing the temperature from 600 °C to 900 °C resulted in a fourfold decrease in sodium cyanide concentration under otherwise constant conditions. A regression equation was derived to express the dependence of sodium cyanide concentration on gasification temperature and reaction duration.

The findings demonstrate that sodium cyanide generation via coal gasification under laboratory condi-tions can yield solution concentrations comparable to those employed in gold cyanidation at industrial gold recovery plants. Establishing on-site sodium cyanide generation at gold processing facilities could significantly reduce production costs by eliminating the need for purchasing, transporting, and storing commercial cyanide reagents.

Keywords: coal gasification, dissolution, sodium cyanide production, gold production, cyanidation.

1. Introduction

Cyanidation is considered the most effective gold extraction method, employed in the leaching process within most processing schemes at mining and processing plants (Yarkova, et al. 2017). The extraction of precious metals by cyanidation is based on the interaction of reagents with the minerals in the gold-bearing concentrate, i.e., the property of gold and silver to react with sodium cyanide in the presence of oxygen to form the complex salt $Na[Au(CN)_2]$, which is difficult to decompose but easily soluble in water, according to the Elsner reaction:

$$2Au + 4NaCN + 1/2O2+ H2O = 2Na[Au(CN)2] + 2NaOH \qquad 1$$

The relative selectivity of the solvent, the successful combination of dissolution and precipitation processes for precious metals from cyanide solutions (cementation with zinc dust, sorption on ion exchange resins and activated carbons, etc.), the simplicity of equipment design, and other advantages of cyanidation make it highly effective and productive. This enables the application of this technology not only to concentrates from mechanical enrichment but also to ordinary gold ores and even tailings containing 1–2 g/t of gold or less. Optimal conditions for the cyanidation process are as follows: S:L = 1.5:1 (Solid to Liquid ratio); sodium cyanide concentration for strong solutions – 0.03–0.06 wt.%, for weak solutions – 0.003–0.01 wt.%; pH of industrial solutions – not lower than 10–10.5 (lime is added as a 20% solution to maintain the pH); solution temperature from 10 to 20°C.

There are many methods for obtaining sodium cyanide, but it is mainly produced by neutralizing hydrocyanic acid with aqueous solutions of NaOH or Na_2CO_3. For the production of cyanide salts, gaseous hydrocyanic acid is directed to alkaline absorbers, which are small cylindrical sealed devices equipped with a bubbler with a stirrer and filled with a solution of caustic alkali. The cyanide salt solution is

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filtered and concentrated under vacuum. The precipitated crystals are separated on centrifuges. Then the salt is dried, packaged, and sent to the consumer.

Sodium cyanide, like all cyanides, is extremely poisonous, therefore, there are special requirements for its transportation (which requires a special permit, special vehicles, undamaged containers and packaging) and storage (in a closed vertical position), as well as subsequent dilution to a solution of a specified concentration (Grigorieva, et al. 2018).

The demand for sodium cyanide depends on the nature of the ore being leached and ranges from 0.25–0.75 kg per 1 ton of dry ore (Chugaev, et al. 2020).

Therefore, obtaining a sodium cyanide solution of a specific concentration directly on the production sites of processing plants is relevant. In this work, it is proposed to use synthesis gas, produced by the gasification of coal and the production of gaseous HCN via the conversion of methane with oxygen and ammonia, and the subsequent synthesis of sodium cyanide through the absorption of HCN by a soda solution (Table 1).

Coal gasification is a high-temperature physico-chemical process of interaction between coal and oxidizing gases (O_2, H_2O, CO_2) to produce gases H_2, CO, CH_4 (see table, equations (1)–(5) (Choudhury et al. 2015; Li B. et al. 2020; Musaev et al. 2012; Zhuravsky et al. 2021). The composition and heat of combustion of the gas produced as a result of gasification vary and depend on the intended applications (Vasilkova et al. 2021). The following products can be obtained:

– Fuel gas (for technological and energy combustion) when a larger volume of methane is present and undesirable products of coal semi-coking (oils, resins, phenols) are absent;

– Reducing gas (in the metallurgical industry) – for the direct reduction of iron ore, etc.;

– Synthesis gas (chemical feedstock for the production of methanol, ammonia, liquid fuel according to the Fischer-Tropsch process) at a certain ratio of CO:H_2 and CH_4:H_2, which is achieved by selecting the conditions of the technological process and choosing the composition of the gasifying agent. (Abdulkadir et al. 2019; Donskoy, et al. 2021; Zakorshenny, et al. 2018).

As shown by the thermodynamic analysis of data under equilibrium conditions (Figures 1, 2), coal gasification can be carried out at temperatures above 500 °C (a temperature of 600–800 °C is sufficient to obtain synthesis gas, reactions (1)–(3) (Xu B. et al. 2020). Hydrogen is synthesized during coal combustion in the temperature range above 650 °C (reaction (1)) (Klimovsky et al. 1960).

Methane synthesis from CO and CO_2 (reactions (4), (5)) occurs at gas temperatures at the outlet of the installation below 600 °C. Even lower temperatures are required for the formation of gaseous ammonia (below 200–300 **°C**, reaction 6) (L.P. Chang et al. 2006; Vasilkova. et al. 2021). Hydrocyanic acid is formed during the co-oxidation of ammonia and methane with atmospheric oxygen over the entire temperature range, as is sodium cyanide, which is synthesized during the chemisorption of hydrocyanic acid by a soda solution.

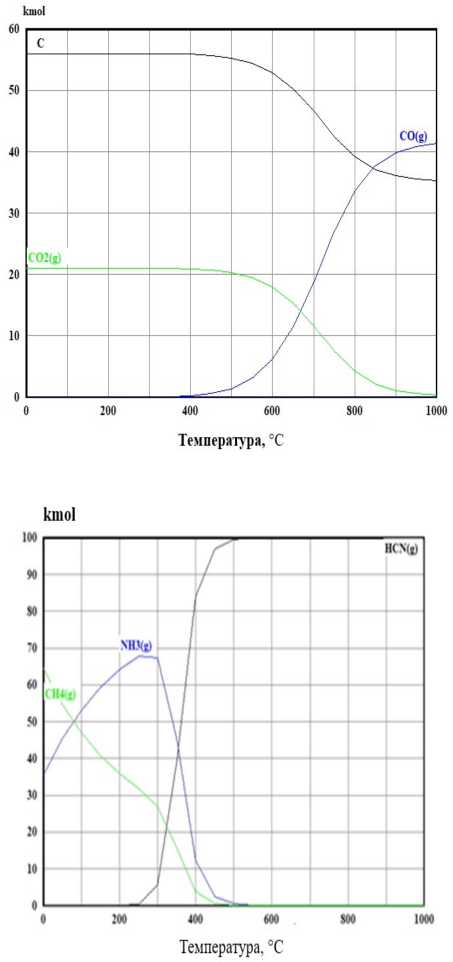

Fig. 1. Influence of the carbon combustion temperature on the synthesis gas composition during coal gasification

Table 1. Stages of reactions during the generation of sodium cyanide

Stage	Reactions	Reaction number	Note
Coal gasification	$C + H_2O(g^*) = H_2(g) + CO(g)$	(2)	The process is based on the interaction of coal with steam. The reaction is endothermic, and the equilibrium shifts to the right starting from 923K.
	$2C + O_2(g) = 2CO(g)$	(3)	In parallel with (2), the exothermic combustion reaction of coal occurs, which provides the necessary heat balance.
	$C+CO_2(g)=2CO(g)$	(4)	The Boudouard reaction. The reaction is endothermic, and the equilibrium shifts to the right starting from 973K.
Synthesis gas conversion to methane.	$CO_2(g) + 4H_2(g) = =CH_4(g) + 2H_2O(g)$	(5)	The equilibrium shifts to the right at temperatures below 873K.
Ammonia formation.	$Ar\text{-}N(s) + H_2(g) = =Ar\text{-}NH_2(s)$ $Ar\text{-}NH_2(s) + H_2(g) = = Ar + NH_3(g)$	(6)	The equilibrium shifts to the right at temperatures below 473K.
Production of hydrocyanic acid.	$2NH_3(g) + 2CH_4(g) + 3O_2(g) = 2HCN(g) + 6H_2O(g)$	(7)	Co-oxidation of ammonia and methane with atmospheric oxygen.
Production of sodium cyanide.	$HCN(g) + NaOH = =NaCN + H_2O$	(8)	Neutralization of hydrocyanic acid with alkali.

*g – gaseous

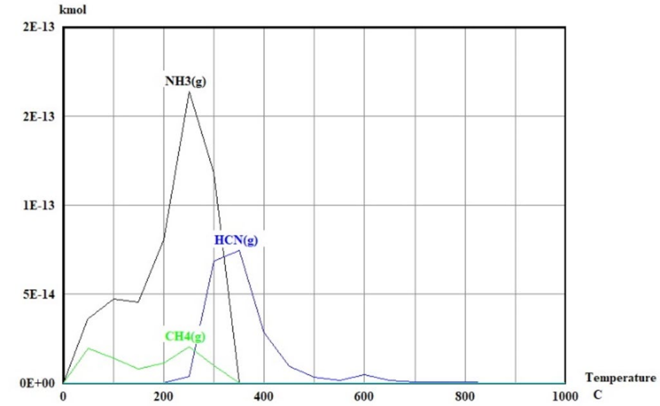

Fig. 2. Influence of the temperature of the exhaust gases on the composition of the synthesis gas during its further sorption with a soda solution

When choosing the temperature regime, it should be considered that the efficiency of absorption increases with a decrease in the temperature of the absorbent. Thus, coal gasification should be carried out in the temperature ranges above 600 °C. However, for the purpose of synthesizing ammonia, methane, and the target product of their interaction, gaseous hydrogen cyanide, followed by effective absorption, a sharp decrease in the gas temperature at the outlet of the installation to 200 °C is necessary, followed by sorption of hydrogen cyanide with a cold alkaline solution.

2. Materials and methods

The laboratory setup consisted of a tubular furnace 1 of cylindrical construction, the body of which was made of heat-resistant steel, lined with heat-insulating bricks, and a series of absorbers. The working section of the furnace was a corundum tube with a spirally wound heating element around it. The temperature in the cell was controlled by a type K thermocouple 4 connected to an OVEN TRM regulator. Before starting the gasifier at the beginning of each experiment, a preliminary check was carried out for leaks, the tightness of the setup, and the operation of the ventilation system. Coal (brown or wood, 30–60 g), pre-crushed to increase the specific surface area, was placed in a quartz tube 2. Then the tube was placed in the furnace so that the middle part of the tube filled with coal was in the furnace chamber, and the edges of the tube extended beyond the furnace chamber by 10 cm. At one end, the tube was tightly closed with a rubber stopper 3, and at the other end with a stopper with a gas outlet glass tube. The gas outlet tube was connected via a silicone hose to a series of absorbers 5, consisting of two absorbers with a volume of 200 ml and one droplet trap. The absorbers were filled with NaOH solution (pH = 10) to 100 ml, and the series was placed in an ice bath 6, which serves as a cooling element for the best conversion effect. The furnace was turned on and the set temperature was set by the regulator. The gas formed during the combustion of coal was gradually displaced through the system of silicone tubes into the series of absorbers. Gradually cooling down, the gas was methanized and converted to hydrogen cyanide, which, when passing through the system of absorbers, was sorbed by the alkaline solution with the formation of NaCN.

After the experiment, the resulting solutions from the absorbers were poured into dry glass volumetric flasks, hermetically closed with a stopper. The flasks were labeled with the name of the product, the time of sampling, and the inscription “Caution - Poison!” and sent for analysis to determine the content of sodium cyanide in the solutions. The content of sodium cyanide in the solution was determined by the titration method in accordance with GOST 8464-79. The HSC Chemistry 5.1 software package was used for thermodynamic calculations. Data analysis was performed using the program STATISTICA

3. Results and discussion

Chang et al. systematically examined the fate of fuel-nitrogen during the steam gasification of brown coal in a drop-tube reactor between 600 and 900 °C and showed that the availability of hydrogen radicals generated from the water-gas reaction ($C + H2O \rightarrow CO + H2$) is the controlling factor for converting char-bound nitrogen to ammonia, whereas hydrogen cyanide forms mainly through the secondary cracking of volatile fragments at the higher end of this temperature window (L.P. Chang et al. 2006). Their results revealed an NH3 yield maximum near 800 °C and a monotonic rise in HCN with temperature – yet HCN remained an order of magnitude less abundant than NH3. Increasing the steam partial pressure (and thus the H-radical pool) markedly enhanced NH3 formation but had only a minor influence on HCN. These observations underpin the present work: they confirm that, within the 600–800 °C zone adopted for gasification, NH_3 and small quantities of HCN are the primary volatile N-species liberated from coal, and that prompt quenching of the product gas is essential to conserve the nascent HCN for subsequent absorption in the ice-cooled alkaline scrubber – thereby maximising the recovery of sodium cyanide In the case of lignite and wood coal where nitrogen content in those raw materials are significantly higher, the production of ammonia and consequently hydrogen cyanide is higher. However, it needs to be mentioned high temperatures lowers the yield of reaction (8) since this exothermic reaction is favorable at lower temperatures, that is in good agreement with the data reported in the literature (J.M. Rogers & H. F. Porte, 1987).

The activation energy of the coal gasification process is calculated using the graphical dependence of the velocity logarithm (lnV) on the inverse temperature (1/T). The obtained activation energy value of 37-39 kJ/mol shows that this process is limited by the absorption of gaseous hydrogen cyanide (HCN) by a soda solution. It follows that one of the main tasks of accelerating the process of sodium cyanide generation during coal gasification is a sharp decrease in the temperature of the synthesis gases by the refrigerator and the lowest possible temperature of the absorbent (soda solution).

It has been found that with an increase in temperature from 600 to 900 °C, the concentration of sodium cyanide in the alkaline solution decreases by almost 4 times with the same duration of the experiment (Figure 3). The obtained concentrations of sodium cyanide when gasifying wood coal in the temperature range of 600–800 °C of 0.03–0.08% mass. correspond to the required concentrations of sodium cyanide in the solution for intensive cyanidation.

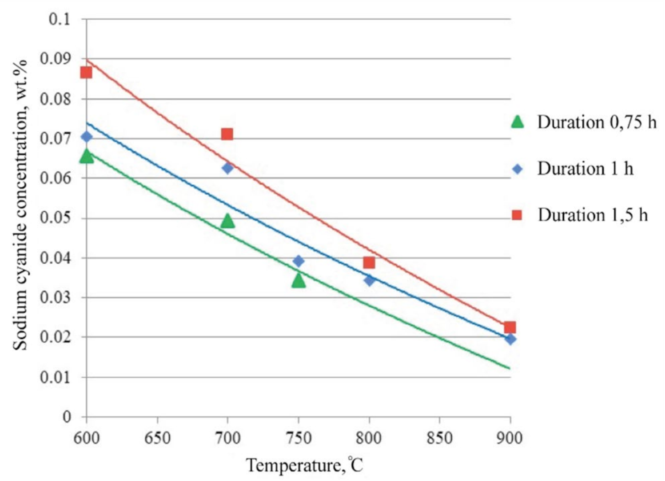

Fig. 3. Effect of the duration and the temperature of the coal gasification process on the concentration of sodium cyanide

As a result of processing the data obtained from the experiments, a regression equation was derived for the dependence of the concentration of sodium cyanide in the alkaline solution on the coal gasification temperature T (°C) and the process duration t (h):

$$C_{NaCN}=0.171 - 2\cdot 10^{-4}\cdot T + 0.023\cdot t.$$

The multiple correlation coefficient is 0.973. The equation is valid in the temperature range from 600–900 °C and within the process duration from 45 minutes to 1.5 hours.

A slight influence of the type of coal used for gasification on the final sodium cyanide content was also noted. Thus, at 700 °C, the sodium cyanide content during the gasification of lignite for 1 hour was 0.04% by weight, while under identical conditions during the gasification of wood coal, it was more than 0.06% by weight. This is due to the fact that wood coal has a lower ash content, less bituminous volatile matter, sulfur, and water than lignite. Also, wood coal has a larger BET surface area due to a large number of capillaries and pores, which is confirmed in the works.

Conclusion

Thus, the results of experiments showed that the generation of sodium cyanide in laboratory conditions by gasification of coal allows, with optimal process parameters, to obtain sodium cyanide concentrations in the solution corresponding to those used at gold recovery plants for cyanidation. As sorption equipment for capturing components of synthesis gas, several stages of gas purification equipment described in (Druzhinin et al. 2020) are proposed.

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