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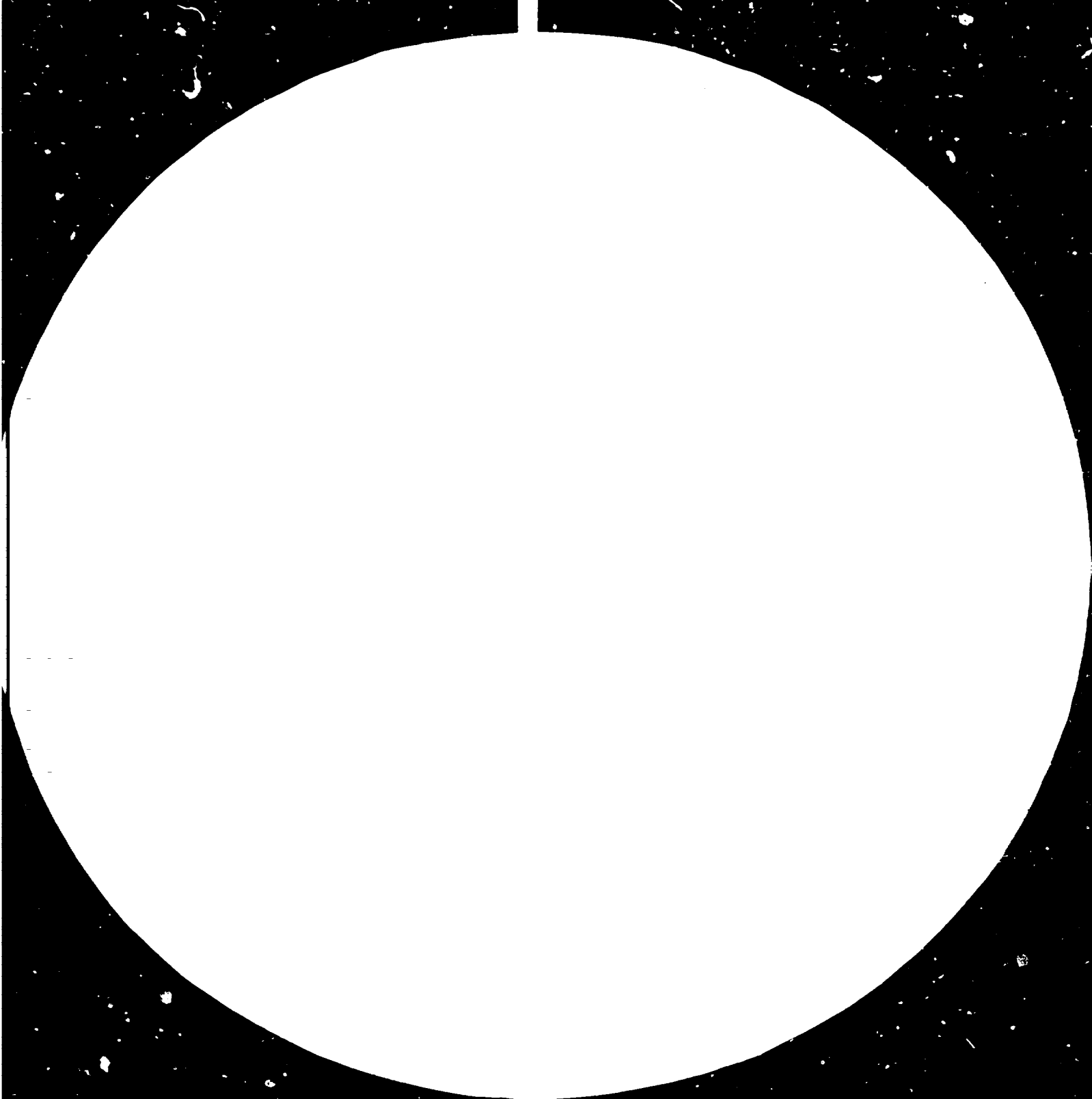
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THE PREPARATION AND GASIFICATION OF CARBONATED
LIME COAL BRIQUETTES*

by

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Abstracts

The carbonated lime coal briquettes are successfully and widely employed for making syngas by ammonia plants in China.

High quality briquettes are obtained by formation of coal fines with slaked lime as binding agent followed by carbonation by means of carbonating gas with controlled CO₂ content at given temperature, moisture and flow rate.

The carbonated lime coal briquettes thus formed are of adequate mechanical strength, good thermal stability and rather high chemical reactivity. In order to meet the specific feedstock requirements of fixed bed gasifiers, briquettes with enhanced ash fusion point can be produced through appropriate adjustment of the coal to lime ratio.

The same gasification technology, namely high temperature, high air space velocity and short cycle in the gasifier, can be adopted for high quality carbonated briquettes just as for the high quality lump coal. The entrained particles do not exceed 5%. Because of the large amount of ash slag it is essential to facilitate the slag removal by improving the grate design and slag discharge mechanism, particularly to operate with thin ash layer.

The semi-water gas produced from carbonated lime coal briquettes contains $\geq 63\%$ CO + H₂ as reactive components, being suitable as a syngas for ammonia production.

1. Introduction

The ammonia production in our domestic plants with a capacity of less than 100 tons per day is mainly based on semi-water gas manufactured from the anthracite or coke in fixed bed gasifiers.

The fixed bed water gas generators call for lump coal of 13~60 mm in size, with satisfactory cold mechanical strength, thermal stability and ash fusion point.

As such sort of lump coal accounts for only about 20~30% of the total coal mined and is far from enough to meet the demands from ammonia industry, the investigation on briquetting coal fines and on utilization of briquettes was started early in fifties in China.

Since most of the anthracite has a poor binding property, some binding agent is required to increase its mechanical strength.

Usually the briquettes manufactured with binding agents such as waste pulp and coal tar show satisfactory mechanical strength in cold state, but their

mechanical strength in hot state is poor due to the presence of organic matters in binding agents which tend to burn in gasifiers, giving entrained matters as high as 10 - 20%.

In early sixties, the mechanism of formation of carbonated briquettes from anthracite fines with slaked lime as binding agent, briquetting and carbonation technology etc... were systematically studied in this country and the briquettes were successfully tested for small size blast furnaces and gasifiers. Later we effectively carried out experiments on carbonated coal briquettes as feedstock for ammonia production. At present carbonated coal briquettes are employed as raw materials for making crude syngas in more than 600 ammonia plants in our country, each with a capacity below 100 tons per day.

The main technical data for the gasification of carbonated coal briquettes are as follows:

1. Carbonated coal briquettes

Compression strength ≥ 60 Kg/single briquette
ash fusion point (T_2) $\geq 1250^\circ\text{C}$
fixed carbon content $\geq 50\%$

2. Semi- water gas

$\text{CO} + \text{H}_2 \geq 63\%$

Gas productivity ≥ 2.7 standard m^3 , semi-
water gas/ Kg of standard coal *.

Gasification intensity $\geq 700 \text{ M}^3$ standard
semi-water gas/ m^2 hour.

*The standard coal is referred to as the coal containing 84% C.

II. The behaviours of carbonated lime coal briquettes
Significant changes in behaviours were observed with carbonated lime coal briquettes compared with original coal, due to the introduction of slaked lime, namely:

1. The higher mechanical strength and thermal stability.

The compression strength of carbonated lime coal briquettes could reach 50-80 Kg/single briquette. When they were first formed, the mechanical strength of green briquettes was only 2-4 Kg/single briquette. Through carbonation, the slaked lime originally dispersed in briquettes became a very strong CaCO_3 matrix, thus increasing their mechanical strength remarkably. Furthermore, part of SiO_2 in the coal ash reacted with Ca(OH)_2 to form calcium silicate hydrate in the presence of water and heat. Its mineral composition was identified as $\text{CaO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$ with X-ray. The formation of such agglomerated structure partly contributed to the increment of the mechanical strength of carbonated coal briquettes.

The carbonated lime coal briquettes has not only high mechanical strength, but also good thermal

strength. This can be accounted for by the fact that the calcium oxide matrix formed from decomposition of calcium carbonate at 800°C in the gasifier retains some mechanical strength. Even after the decomposition of calcium carbonate upon heating the briquettes still show a mechanical strength of 40 Kg/single briquette, with their appearance being intact. In addition, there are other components such as $\text{SiO}_2\text{Al}_2\text{O}_3$, etc..in briquettes. These substances will react with CaO at the temperature of the gasifying zone to form silicates having mechanical strength.

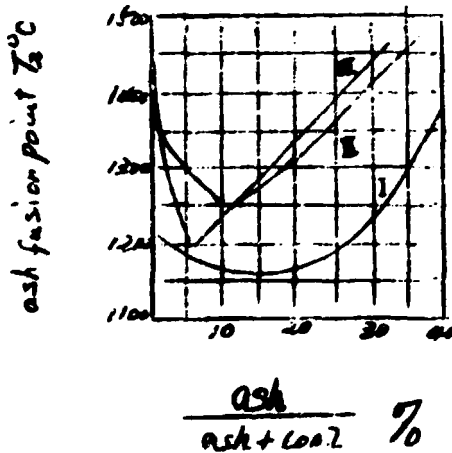
2. The higher ash fusion point resulting from adjustment of the ratio of coal to slaked lime.

To ensure the higher gasification efficiency for batchwise fixed bed gasifiers, the feedstock coal with higher fusion point is required. Generally the softening temperature (T_2) of coal ash should not be lower than 1250°C.

Pure calcium oxide presents very high melting point. When it is blended with coal fines to form briquettes, the elemental carbon burns off during a high temperature gasification while the remaining ash together with lime form a kind of eutectic substance.

The ash fusion point of carbonated lime coal

briquette is closely related with the composition and content of ash and the amount of lime added into briquettes. For anthracites with acid ash the melting points of the eutectic substance tend to fall to different extents when slacked lime is first added. After the lowest eutectic point is reached the ash fusion point begins rising with the increment of lime. For different types of coal the introduction of lime changes the melting points and curve slopes differently as in Fig. 1.



- I. Longyan mixed coal
- II. Hongguao coal
- III. Koayuan

Fig. 1. The relationship between lime/coal ratio and ash fusion point

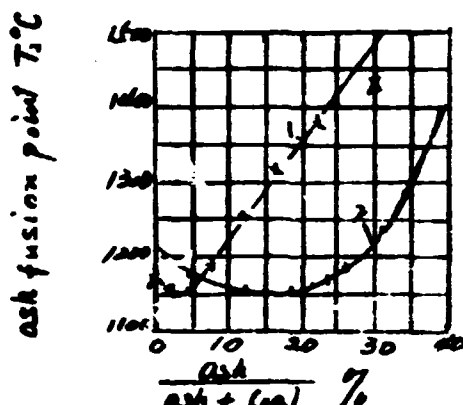


Fig. 2. The relationship between
lime/coal ratio and ash
fusion point.

Fig. 2 shows the tendency of ash fusion point curves for two coal samples of identical type but with different ash content and different amounts of lime introduced. Obviously when the same amount of lime, e.g. 20%, is added, the ash fusion temperature (T_2) of the sample with higher ash content is 1180°C, while that of the sample with lower ash content is 1350°C. It may be concluded that the ash fusion points of briquettes are related to the ash contents of original coals. For a given amount of lime the relationship between the ash fusion point of rich - calcium - oxide ash and its chemical composition can be expressed by alkalinity "K":

$$K = \frac{\text{CaO} + \text{HgO} + \text{Fe}_2\text{O}_3}{\text{SiO}_2 + \text{Al}_2\text{O}_3} \quad (\%, \text{ by weight}) \quad (1)$$

when K value falls within the range of 0.42 - 1.82, or $T_2 = 1150^\circ - 1450^\circ\text{C}$. its function approaches to a straight line, so it can be represented by linear equations:

$$\text{R.D.}(T_2) = 202 K + 1061^\circ\text{C}$$

$$\text{R.D.}(T_3) = 191 K + 1088^\circ\text{C}$$

Furthermore, the quantity of lime required can be calculated.

assuming

W_1 = ash weight

W_2 = weight of slaked lime

A_1 = acidic oxides in ash ($\text{Al}_2\text{O}_3 + \text{SiO}_2$)%

A_2 = acidic oxides in slaked lime ($\text{Al}_2\text{O}_3 + \text{SiO}_2$)%

B_1 = alkaline oxides in coal ash ($\text{CaO} + \text{MgO} + \text{Fe}_2\text{O}_3$)%

B_2 = alkaline oxides in slaked lime ($\text{CaO} + \text{MgO} + \text{Fe}_2\text{O}_3$)%

hence

$$K = \frac{W_1 B_1 + W_2 B_2}{W_1 A_1 + W_2 A_2}$$

$$\text{or } \frac{W_2}{W_1} = \frac{\text{Weight of slaked lime}}{\text{weight of coal ash}} = \frac{KA_1 - B_1}{B_2 - KA_2} = R \quad (3)$$

For a given type of coal and lime, the composition is determined by analysis the alkalinity K corresponding to the desired ash fusion point (T_2) of briquettes is calculated by using Equation (2). By substituting K into equation (3) the ratio (by weight) of lime to

coal ash (R) is obtained. Hence the necessary percentage of lime X^{L} is calculated from the ash content A^{L} in coal fines:

$$X^{\text{L}} = \frac{100 R A^{\text{L}}}{100 + R A^{\text{L}}} \% \quad R = \frac{100 X^{\text{L}}}{(100 - X^{\text{L}}) A^{\text{L}}} \quad (4)$$

It can be seen from the equation that if lime to coal ratio X^{L} is fixed the less the ash content A^{L} in the coal, the greater the R value, hence the higher the alkalinity K and the ash fusion point (T_2) of briquettes. Therefore the selection of coal with low ash content is of great importance to raise the ash fusion point of the carbonated lime coal briquettes.

3. The higher chemical reactivity

The chemical reactivity (as an indication of CO_2 conversion rate) of carbonated lime coal briquettes is 1-3 times higher than that of the lump coal of the same type as shown in Fig. 3.

The measured relative porosity of carbonated lime coal briquettes was 10 times higher than that of the lump coal. Consequently, the carbonated lime coal briquettes demonstrated an extended surface area in favour of the reaction of molecules between gas and solid phases, which in turn resulted in the improved chemical reactivity of briquettes.

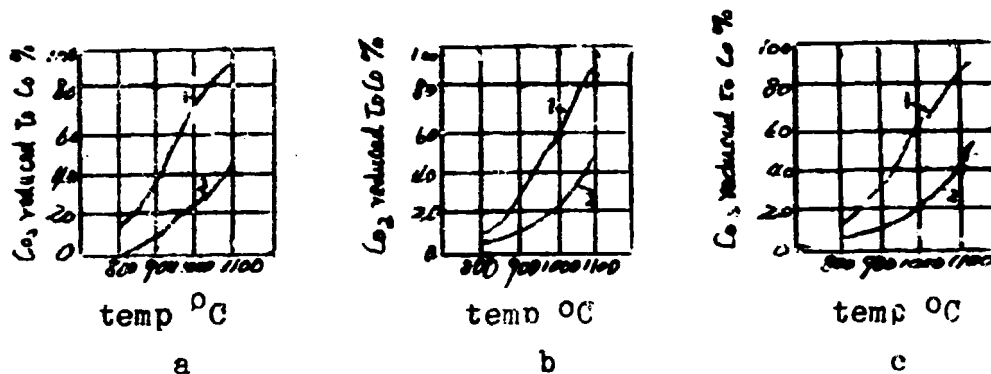


Fig. 3. The composition of chemical reactivity between the carbonated lime coal briquettes and the original coal of the same type.

- a) Fujian Longyan coal.
- b) Guangxi Hongmao coal.
- c) Fujian Tainhushan coal.

The catalytic activity of the slaked lime in briquette is another important factor accounting for the chemical reactivity of briquettes.

The studies on gasification of carbonated lime coal briquettes and catalysis in the shift conversion showed that for C-H₂O reaction the rate of carbonated lime coal briquettes is 2 times faster than that of the lump coal of the same type; and for C-CO₂ reaction 1.3 times faster. Probably the main reasons for the high chemical reactivity may be the catalytic activity of CaO-CaCO₃, which, however, becomes standing out only for the system of intimate contact between CaO - CaCO₃ and C.

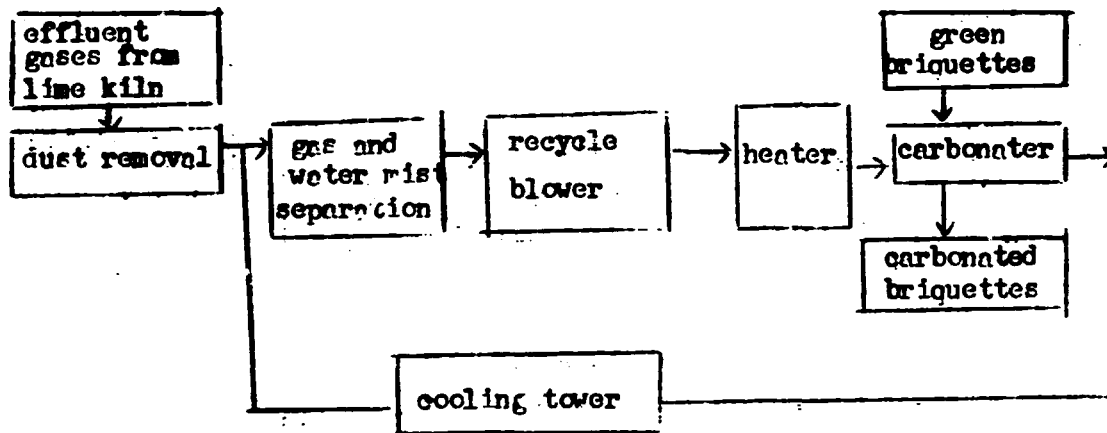
As far as the catalytic activity of lime in carbonated briquettes for the shift conversion of water gas is concerned, the max. CO shift rate close to the theoretical value is reached at the temperature of 600 C, if $H_2O/CO = 4$.

4. The decrease in fixed carbon content

The introduction of lime into briquettes inevitably leads to a decrease in the fixed carbon content. In case of the fixed carbon content lower than 45%, however, a remarkable reduction in gasification efficiency will occur. If ash content in anthracite exceeds 25% screening and washing should be exerted in order to reduce the ash content and to impart the carbonated lime coal briquettes with good mechanical strength, high ash fusion point and high carbon content.

III. The preparation of carbonated lime coal briquettes

The preparation of carbonated lime coal briquettes comprises two steps: One is compounding and formation; the other is carbonation and hardening. The process can be outlined by the following scheme:



The compounding of raw materials, i.e. the amount of introduced slaked lime should satisfy the mechanical strength and ash fusion point requirements of briquettes and meanwhile maintain an adequate fixed carbon content. The accurate compounding and uniform blending of coal fines and slaked lime are prerequisites to make the quality of briquettes consistent.

The water content needed for coal briquettes formation is usually controlled within the range of 9 -11% and the cage type pulverizer is used for crushing and blending. The raw materials of adequate fineness are fed into a dual roll briquetting press which gives briquettes weighing about 30-45 grams each. The improvement of the compactness of the lime coal briquettes is accompanied by the enhancement of their thermal

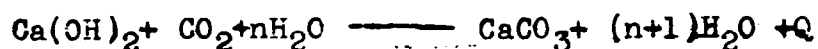
mechanical strength. The compactness of briquettes can be indicated by the compression degree (or compression ratio):

$$\text{Compression ratio} = \frac{\text{apparent density of green briquettes}}{\text{bulk density of coal fines}}$$

Usually the compression ratio is kept above 1.4.

The mechanical strength of green briquettes is relatively low and it must be further improved by carbonation.

The carbonation proceeds according to the equation



Approaches through which the CO_2 diffuses inside the briquettes were studied by means of radio - active C^{14} tracer. The surface of the sample was carbonated first with radio - active C^{14}O_2 and then with C^{12}O_2 for further carbonation. The results showed that C^{14}O_2 , deposited on the briquette surface did not move into its inner part. This meant that the gaseous CO_2 diffused into the inner part of the briquette continuously during the whole carbonation process.

In carbonation the diffusion of CO_2 into briquette core is a rate-determining step.

The carbonation of green briquettes must be carried

out in the presence of water. Inadequate water will adversely affect the carbonation, while excessive water will encumber the diffusion of CO_2 into the inner part of briquettes. Normally the porosity of briquettes is about 25%, and the water content of green briquette is about 10% which occupy more 60% of the porous space of the briquette. The water formed during carbonation will take up the additional portion of porous space. Therefore the excessive water should be continuously removed to ensure that the carbonation runs smoothly.

Fig. 4 shows that either excess or inadequacy of water will impair the mechanical strength of briquettes.

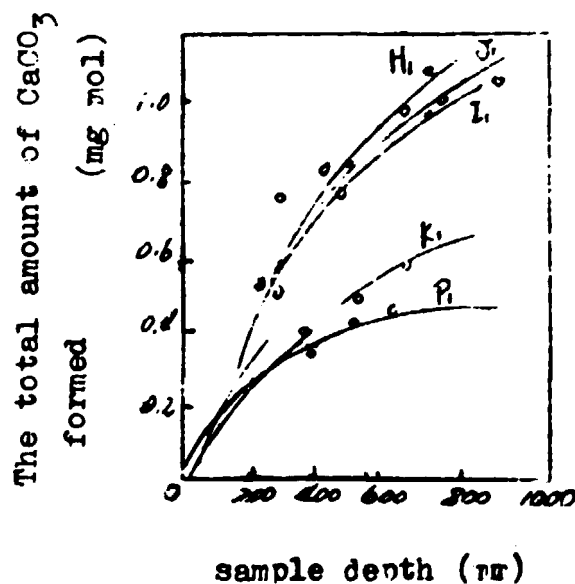


Fig.(4). The relationship between the water content and the abrasion strength of briquette.

It can be seen from Fig. (5) that whenever the water content was above 8%, the diffusion of CO_2 into the inner part of the briquettes was hindered and less CaCO_3 was formed due to the blockage of passages by the excessive water. If the water content was reduced to 4%, the diffusion of CO_2 was facilitated with optimum carbonation results obtained.

Therefore the removal of excessive water by pre-drying prior to carbonation will improve the efficiency of the carbonation.

The rapid drying may result in a gradient distribution of water along passages through which the CO_2 diffuses into the inner part of briquettes, thus reducing the resistance against the diffusion of CO_2 and improving the carbonation efficiency.

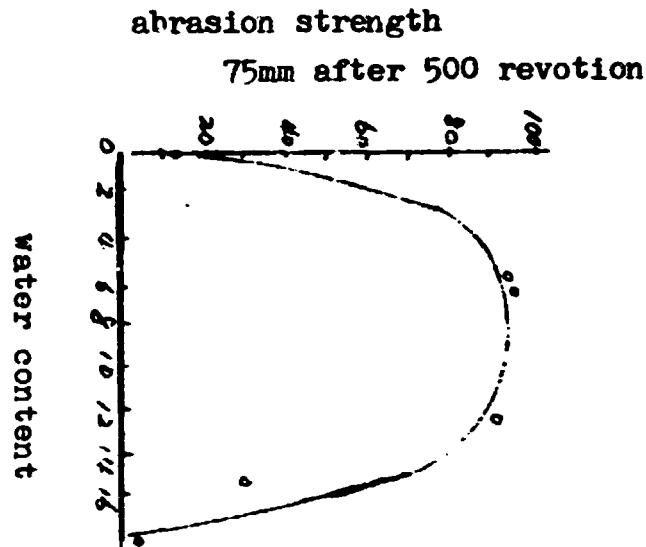


Fig.(5) The relationship between the degree of carbonation and the water content coke fines 70%, line 30%, normal pressure, ambient temperature

P_1 water = 14% , K_1 water = 8% , H_1 water = 4%;

I_1 the water distribution gradient along the diffusion of CO_2 : 0.4,6,10 (%);

J_1 the water distribution gradient along the diffusion of CO_2 : 4,8,10,14 (%)

(The sample depth indicates the distance between the surface and the place where the sample is taken.)

The carbonation of briquettes is affected by the concentration of the CO₂, the temperature, the humidity and the flow rate of the carbonating gases. High CO₂ content is beneficial to the carbonating reaction. Even in case a gas with low CO₂ content such as industrial waste gas is used as a carbonating gas, good carbonation results can also be attained by increasing its flow rate. An excessively high temperature or a too low humidity of the carbonating gas will cause the water content in the briquette to evaporate off vigorously, thus hindering the diffusion of CO₂ into the inner part of the briquette. The loss of water required for the carbonation process will result in extremely poor carbonation efficiency. In this case merely more dried coal briquettes with low mechanical strength are used. Both tests and actual practice have shown that the carbonation temperature of about 80°C is preferred.

Based on the mass and heat-balance, for one ton of carbonated briquettes 30 -- 40 standard m³ of CO₂ are needed and 90 -- 100 Kg of water are to be evaporated. To remove such a quantity of water in addition to the heat of carbonation 40,000 kcal from other source should be supplemented. The increase in the flow of carbonating gas will bring in more heat

and carry out more water, thus shortening the carbonation time.

At present, cylindrical retort type carbonators are used most widely in our country. They feature simple structure and less investment. Due to the relatively big depth of bed, the carbonation degree of briquettes varies greatly along the axial direction. Both carbonation and drying proceed layer by layer, so the time needed for the completion of carbonation is quite long.

The preparation of carbonated lime coal briquettes can be further improved by modifying either the technology or equipment for carbonation and drying, by shortening the carbonation period, by optimal compounding and by using granulation instead of briquetting.

IV. The gasification of carbonated briquettes

Like superior lump coal, high quality carbonated briquettes can adopt the same gasification technology, i.e. high gasifying temperature, high air space velocity and short operating cycle to achieve a relatively high gasification intensity and gas generation volume.

Since the slight clinkering of ash results in a better gasification efficiency, it is desired to raise

the temperature in gasifying zone just as for the superior lump coal as close as to their ash softening temperature. In case of excessive clinkering, the agglomerates can be broken down by increasing the volume of upward blast steam for a short period of time to facilitate the discharge of clinkers.

The carbonated coal briquettes have relatively high mechanical strength at high temperature, as it was mentioned before, about 1 m/sec. air flow rate can be employed in order to accelerate the heat recuperation. In normal gasification process, the entrained matter does not exceed 5%.

It is important to discharge the coal ash in time and to keep the gasification operation under thin-ash-layer conditions because of the relatively high ash content of the carbonated lime coal briquettes, the thin ash layer has the advantage of not only lessening the resistance against the air flow coming into the gasifier and hence improving the gasifying conditions, but also reducing the caking of slags. The ash layer should be controlled within 10—15 cm. The excessive thinness of the ash layer may cause damage to the grate, so it should be avoided anyway.

Considering the relatively high ash content in the carbonated briquettes, the quantity of the upward blast steam should be slightly higher or equal to that of the downward blast steam during gasification. In no circumstances is it allowed to increase the downward blast steam volume as for the gasification of coke. Otherwise it would cause either the change in the gasifying layer or the occurrence of slag caking and other abnormal phenomena.

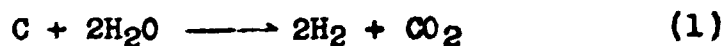
Because of their evenness of sizes the carbonated lime briquettes exhibit low resistance to air flow. When a higher air blowing rate is used, the thickness of the gasifying layer can be greater than that for the lump coal, i.e. as thick as 80 cm. The increase in the thickness of the gasifying layer raises the average temperature of the gasifier increases the heat recuperation of the coal layer and lowers the temperature extreme so that the caking due to local overheat is eliminated.

The carbonated briquettes usually contain more than 30% of ash. Therefore the ash slag discharge load of the rotary grate for carbonated briquettes is much higher than that for lump coal or coke. So the grate design needs to be modified in favour

of the crushing and discharging. Further more the CaO contained in the ash is liable to cake in the presence of water and heat, thus hampering the rotation of the grate. Appropriate measures should be taken to prevent the blockage of the chute caused by the ash slag adhering to the gear.

The semi-water gas ($\text{CO} + \text{H}_2$) generated from carbonated briquettes can be used as a syngas for the production of ammonia. Compared with the gases produced from the lump coal or coke, however, it is 5% lower in active component content, but 7—9% higher in CO_2 content. Therefore, the reasons for the increment of CO_2 are as follows:

1. The gasifying temperature of carbonated briquettes is slightly lower than that of lump coal, which gives rise to more CO_2 formed.



2. The CO formed will react with steam



The extent of reaction (1) is related to the chemical reactivity of carbon, while the shift reaction of the water gas (2) to the catalysis.

As it is mentioned in the foregoing section, the carbonated briquettes exhibit not only higher chemical reactivity than that of the original coal, but

also catalytically affect the shift reaction of water gas. This is why the semi-water gas contains more CO_2 .

Thanks to the higher content of CaO , ash slag from the gasification of carbonated briquettes can be utilized as a raw material for making bricks or silicate cement.

Table 1. The operation specifications for briquette formation and carbonation.

Table 1. The operation specifications for briquette formation and carbonation

item	unit	lime kiln gases pro- cess	
input of slaked lime	%	25-30	
water content in fine materials	%	8-11	
weight of briquette	g/piece	30-45	
carbonating gas pressure	Kg/cm ² (g.p.)	0.1-0.2	
CO ₂ concentration in the carbonating gas	%	25-30	
flow rate of carbonating gas	NM ³ /hour. M ³ briquette	120-150	
carbonating time	hour	17-20	
temper- ature	incoming carbonating gas	°C	110-130
	effluent gas during carbonation	°C	45-50
	effluent gas at the end of carbonation	°C	80-90
quality of briquet- te	carbonation percentage	%	> 85
	compression strength	Kg/ single briquette	> 60
	ash fusion point (T ₂)	°C	>1250

Table 2. The controlling data for normal operation of a ϕ 2260 gasifier

item	unit	data	
sectional area of the gasifier chamber	M ²	4	
inlet air volume	M ³ /hour	10,000-14,000	
air blast rate	M/sec	0.7-1.0	
air blast pressure	m.m. H O	18,00-2200	
steam upward blast	ton/hour	~ 2.6	
flow downward blast	ton/hour	~ 2.8	
temperature of gasifier	top	°C	~ 450
	bottom	°C	~ 160
gasification recycle time	sec	~ 150-180	
briquette feeding cycle	min.	30-35	
briquette feeding quantity each time	Kg	800-900	
thickness of carbon layer (including ash slag)	M	1.7-2.0	
thickness of ash layer	mm	100-150	
ash discharge cycle	times/shift	3-4	
composition of semi-water gas	CO ₂	%	12-15
	CO	%	23-26
	H ₂	%	38-42
	N ₂	%	18-20
	O ₂	%	0.3-0.5
	CH ₄	%	~ 1.0
gas generation volume	M ³ /hour.unit set	2500-3000	

