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CYANIDES IN FeCr SUBMERGED ARC FURNACE PRODUCTION. THEORETICAL AND PRACTICAL CONSIDERATIONS

H. Jalkanen[1], M. Kojo[1], H. Krogerus[2], P. Niemelä[3], P. Oikarinen[4],
[1] Helsinki University of Technology, Espoo, Finland
[2] Outokumpu Research Oy, Pori, Finland
[3] Outokumpu Chrome Oy, Tornio, Finland
[4] Outokumpu Engineering Contractors Oy, Espoo, Finland

ABSTRACT

In a modern FeCr production process, like the Outokumpu process, smelting is performed in a closed submerged arc furnace. In addition to the main components, the furnace charge contains some amount of nitrogen and alkalies which can form stable cyanide species with carbon. High temperature and reducing conditions are favourable for cyanide formation. The formation and stability of cyanides under furnace conditions were studied by thermodynamical calculations. The results indicated that cyanides can be present in the gas phase in reductive atmosphere at temperatures above 800 °C. Laboratory tests showed that a remarkable amount of active organically bonded nitrogen is brought into the process with coke and electrode paste. In addition, it was proved that alkalies increase the cyanide formation. The cyanide levels detected in the furnace atmosphere in the Outokumpu Chrome FeCr furnace were in agreement with the theoretical values. The furnace gas is washed in two venturi scrubbers where the cyanides enter into the washing water. The calculations as well as the measurements showed that cyanide compounds are not stable in washing water at temperatures of 25-100 °C. In the Tornio works, the washing water is used in slag granulation where the main part of the cyanides decomposes. About 90 % of the waters are recirculated in a closed circuit. In the waste waters the cyanide levels are well below permissible limits.

INTRODUCTION

The global demands for environmental protection are being tightened all the time. As a producer and technology supplier, this is a challenge for the Outokumpu group. Environmental aspects are taken into account in all process development stages to minimize environmental risks. It is important to understand the theoretical aspects of the formation mechanism of the harmful components to eliminate possible emissions by a proper process design or by raw material selection.

In a modern ferrochrome process, like the Outokumpu one, smelting is performed in a closed submerged arc furnace. It has been stated that the high temperature and reducing conditions in the furnace are favourable for cyanide formation. Outokumpu has been making investigations on the subject during two decades. A larger investigation programme of the formation and behaviour of cyanides in ferrochrome smelting was carried out in 1991-92 in co-operation with Outokumpu Chrome, Research and Engineering and the Helsinki University of Technology [1]. Theoretical thermodynamical calculations on the formation of cyanide species were first made as the basis for the investigations. Plant measurements carried out at the Outokumpu Chrome Tornio works consisted of determination of the amount of cyanides in samples taken from the 75 MVA ferrochrome furnace. The samples were taken from furnace gas, venturi scrubber water and circulating water. Final thermodynamical calculations were made based on material balance and exhaust gas analysis from the measurements. The role of alkalies on the formation of gaseous cyanides was confirmed in the laboratory tests. This paper summarizes the results of the investigations.

OUTOKUMPU FERROCHROME PROCESS IN TORNIO

The ferrochrome process at Tornio Works consists of pelletizing and sintering chromite concentrate in the steel belt sintering plant, and smelting the mixture of pellets and upgraded lumpy ore with coke and fluxes in a closed submerged arc furnace. The smelting batch is preheated in a shaft type preheating kiln before smelting, the kiln being located above the smelting furnace. The CO-rich gas, 85 % CO, formed in the smelting furnace, is cleaned in two venturi scrubbers and gathered in a gas receiver. The gas is utilized as fuel in several process units in the ferrochrome and steel works. The process flow sheet is presented in Fig. 1.

Since production started in 1968, Outokumpu has used closed furnaces with preheated charge. With sintered pellets and preheated charge, the specific electric energy consumption is low, thus the process is economical and non-polluting. The CO-gas is high quality fuel with very low sulphur content. Because the off-gas volume from smelting is small and utilized in other processes the dust emissions into the atmosphere are minimized.

The process is a totally closed system also in the sense that 90 % of the waters are recirculated in a water treatment system. After clarification of the scrubbing sludge the water is used in the granulation of the slag. Finally, the water is led into settling ponds. Only 10 % of the circulating water is led to the sea with contaminants way under the stringent permission limits.

RAW MATERIALS AS CYANIDE SOURCES

The raw materials contain some amount of nitrogen and alkalies which, according to theoretical examinations, can stabilize gaseous cyanide species. The content of some affecting minor elements in the raw materials is presented in Table I, and the distribution of the same elements in the charge in Table II.

The amount and analyses of volatiles of coke and electrode paste were measured in the laboratory by heating and gathering the released gas into absorption flasks. Water soluble CN^- and NH_4^+ were measured. The amounts of these species from coke were negligible, but in the electrode paste the corresponding values were about 40 mg/kg paste and 127 mg/kg paste.

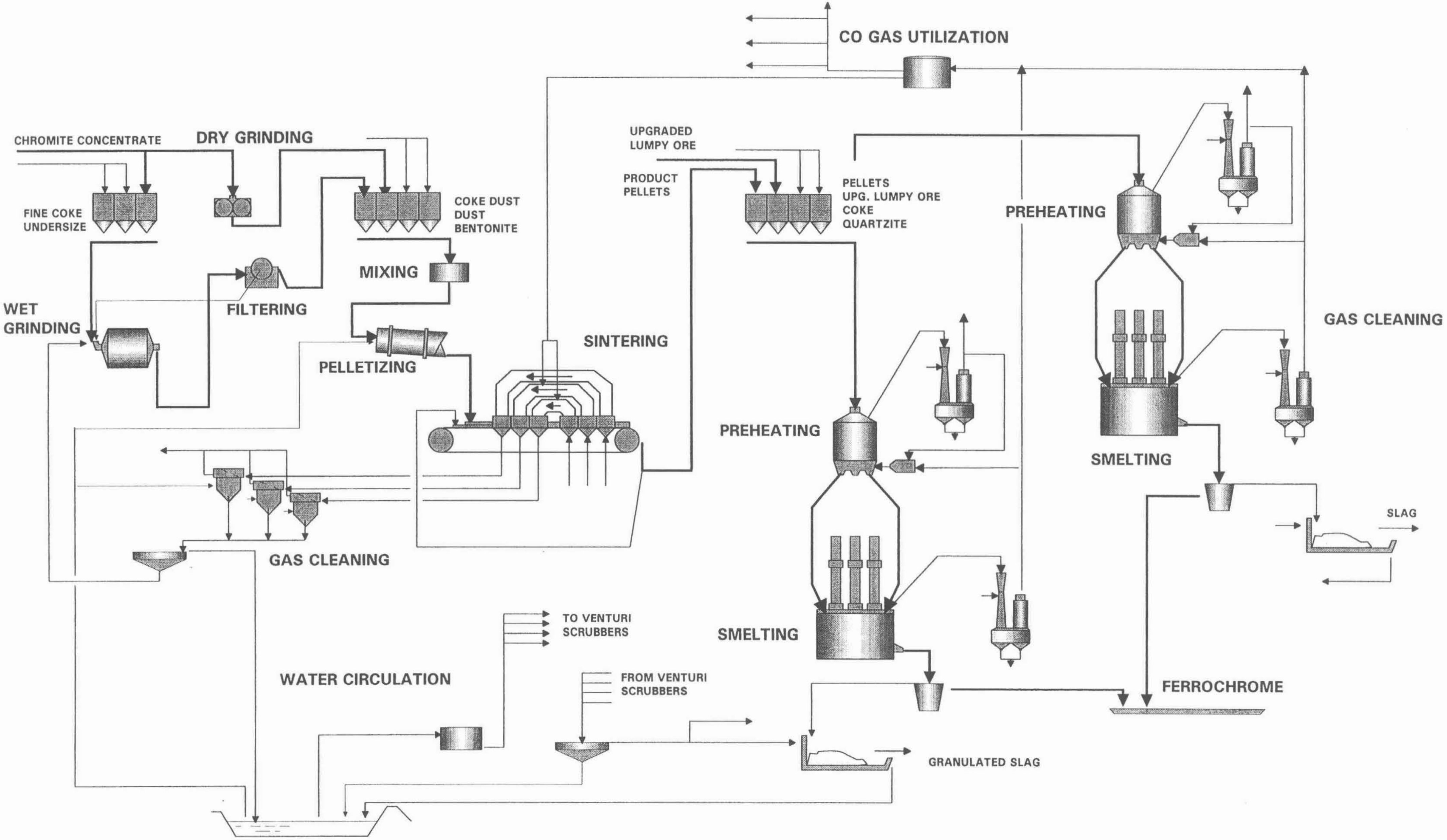

FIG. 1. **Outokumpu Ferrochrome Process at Tornio Works.**

TABLE I. Contents of sodium, potassium and nitrogen in raw materials.

	Na wt-%	K wt-%	N (tot) wt-%
Pellets	0.025	0.010	0
Upgraded lumpy ore	0.05	0.05	0
Cokes	0.07-0.15	0.11-0.15	1.5-1.9
Quartzite	0.27	1.1	0
Electrode paste	0.028	na	1.2

TABLE II. Weight distribution of sodium, potassium and nitrogen in the furnace charge.

	Na %	K %	N (tot) %
Pellets	15	3	0
Upgraded lumpy ore	30	14	0
Cokes	20	13	98
Quartzite	35	70	0
Electrode paste	0	0	2
Totally	100	100	100
Totally, g/t FeCr	2,000	4,100	6,800

EQUILIBRIUM CONSIDERATIONS

Thermochemical conditions in the furnace - environment for formation of gaseous pollutants

Different phases and temperature fields prevailing in the submerged arc furnaces are schematized in Fig. 2. Several sources report high temperature fields nearest to the electrodes reaching values up to 2500-3000 °C or even higher. At the same time the temperature in furnace atmosphere and surface layers of the burden hardly reaches a thousand degrees centigrade. Thermochemical conditions in the furnace are further characterised by low oxygen and high carbon potential. Normal furnace gas analysis is 85 % CO, 5 % CO_2, 5 % H_2, 4 % N_2 and 1 % H_2O. Preliminary thermochemical calculations showed that, even with the most oxidizing off-gas compositions, conditions are too reducing for the formation of substantial amounts of NO_x or chromium trioxide - equilibrium contents of the mentioned species in the gas will remain under the level of 1 mg/Nm^3. The only serious gaseous pollutants expected to be formed in a closed submerged arc furnace will be the gaseous cyanides and other cyan-species. Therefore the thermochemical considerations, analytical measurements in the ferrochrome smelting furnace and laboratory tests were concentrated on

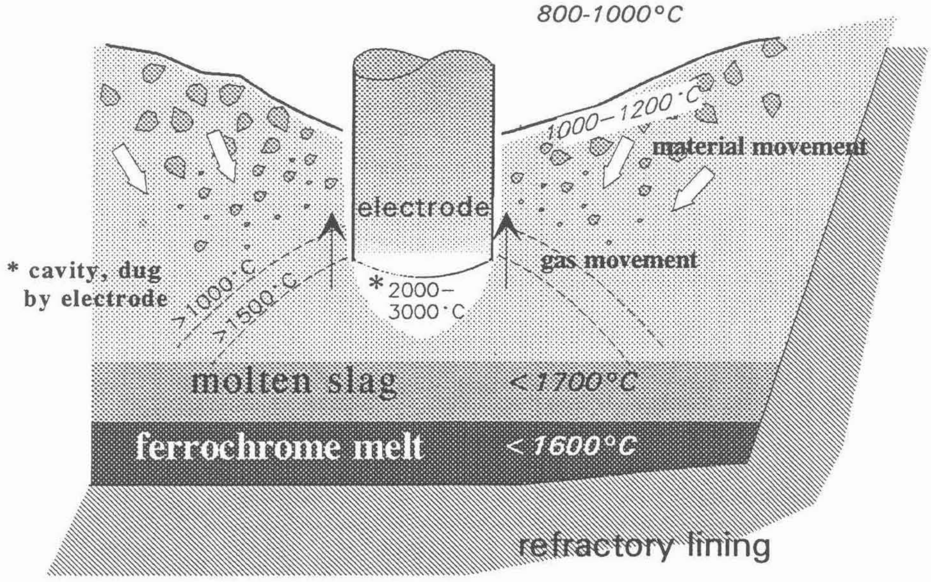

FIG. 2. A schematic illustration of electrode surroundings in the submerged arc ferrochrome smelting furnace. Temperatures of the furnace gas and condensed phases, given in italic numbers, are normal values in the Tornio Works.

the formation and behaviour of cyanides in the furnace atmosphere as well as in the venturi scrubber and recirculating waters.

Equilibrium calculations on the formation of gaseous cyanides

Gas equilibrium considerations were based on a material balance in the submerged arc furnace. The material balance was related to one ton of ferrochrome, with 51 % Cr, 685 Nm^3 furnace gas and 11 kg flue dust being measured to be produced per one ton of ferrochrome. According to the mass balance practically all hydrogen measured in the furnace gas and one fifth of nitrogen, i.e. a total of 6.8 kg, originate from the charged chromite ore, coke and electrode material. In the flue dust all potassium and sodium, 0.57 kg and 0.17 kg per ton of FeCr respectively, and about one third of the magnesium and silicon were considered to be evaporation products - besides the alkalies, the two latter substances seemed to be enriched in the flue dust.

Equilibrium calculations aiming to simulate the formation of cyanides in the burden and electrode environment and their behaviour in the furnace gas were carried out using the thermochemical calculation package HSC Chemistry [2]. All gaseous species formed by C, H, N, O, K, Na, as well as Mg(g) and SiO(g), 94 species altogether, available in the HSC database were included in preliminary calculations aiming to find out the most significant gaseous components. Composition of equilibrium gas computed at carbon saturation (carbon activity is unity relative to graphite) is presented in Fig. 3. The predominating cyanide and cyan species at high temperature regions are HCN, CN and C_2N. Potassium and sodium monocyanides, KCN and NaCN are stabilised by temperature decrease and become predominant cyanide species at around 1000 °C. Further decrease in temperature tends to cause decomposition of alkali cyanides at the expense of gaseous alkali hydroxides.

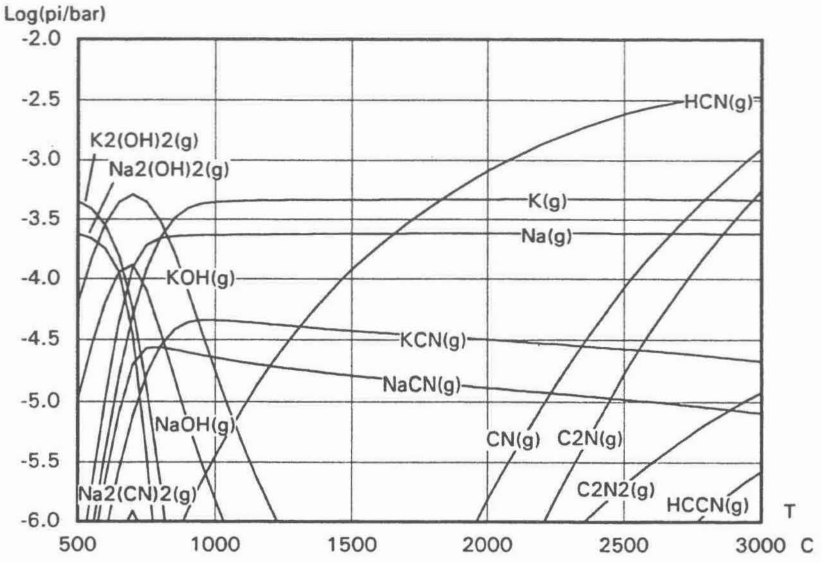

FIG.3. Composition of carbon saturated equilibrium gas.

Calculations showed that a molten mixture of alkali carbonates with insignificant cyanide and hydroxide contents tends to condense from the carbon saturated equilibrium gas mixture at around 900-950 °C, Fig. 4. Salt mixture was treated as a "Temkinian" ideal solution in which the ideal activities of carbonate, cyanide and hydroxide species, A_2CO_3, ACN and AOH are expressed as products of cation and anion fractions $N^2_{A+}\cdot N_{CO3^{2-}}$, $N_{A+}\cdot N_{CN-}$ and $N_{A+}\cdot N_{OH-}$, in which A stands for K and Na, N_{A+} and N_{OH-} for the corresponding cation and anion fraction in the molten mixture.

Another set of calculations was carried out in order to estimate the evolution of gas composition with decreasing temperature if the decomposition of carbonaceous gaseous species and precipitation of solid carbon is restrained, i.e. the Boudouard reaction is suppressed. A gas mixture, formed at 2000 °C in equilibrium with carbon was computed to be cooled down without any carbon precipitation. The result is a metastable gas mixture increasingly oversaturated by carbon with decreasing temperature, see Fig. 5. Carbon activity, (relative to graphite) that at 2000 °C is equal to one, has increased at 1200 °C to 22 and at 800 °C to 45 in the metastable gas mixture. Increasing carbon oversaturation and accordingly carbon potential stabilizes cyanide species, monocyanides at 700 to 1100 °C and dicyanide species towards lower temperatures and no such substantial decomposition of cyanides at the expense of gaseous hydroxide species as for the equilibrium gas mixture tend to proceed. An ideal "Temkinian" molten salt mixture with potassium cyanide as the major constituent was computed to be condensed from the metastable gas at around 850-900 °C.

The mass-action effect of hydrogen, nitrogen and alkali content on the cyanide formation is demonstrated in Figs. 6 to 8, obtained by adding corresponding substances stepwise into the equilibrium gas mixture from 1000 °C and computing the equilibrium composition. An increase in nitrogen and alkali (here potassium) content directly enhance the formation of gaseous alkali cyanides, whereas hydrogen addition cause an increase only in the equilibrium content of hydrogen cyanide which is more than compensated by a decrease in alkali cyanide concentrations.

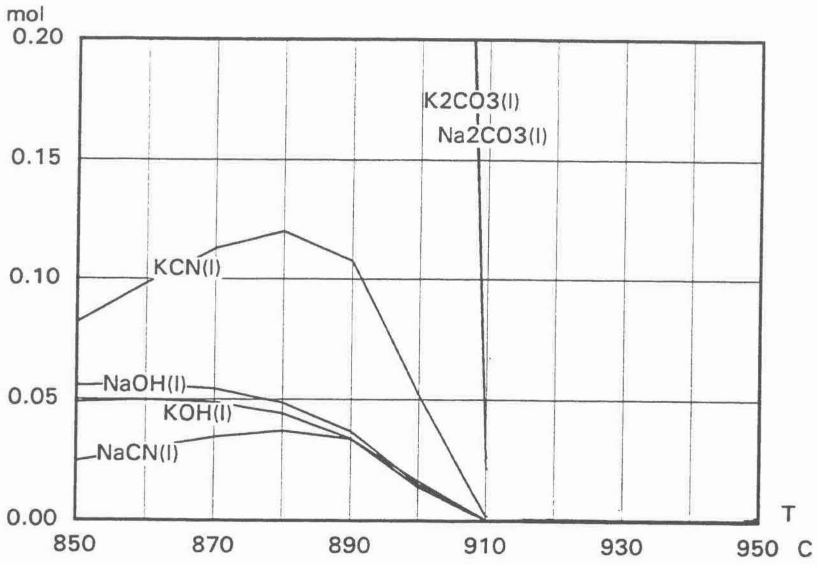

FIG.4. Condensation of (ideal Temkinian) molten salt mixture from the equilibrium gas mixture.

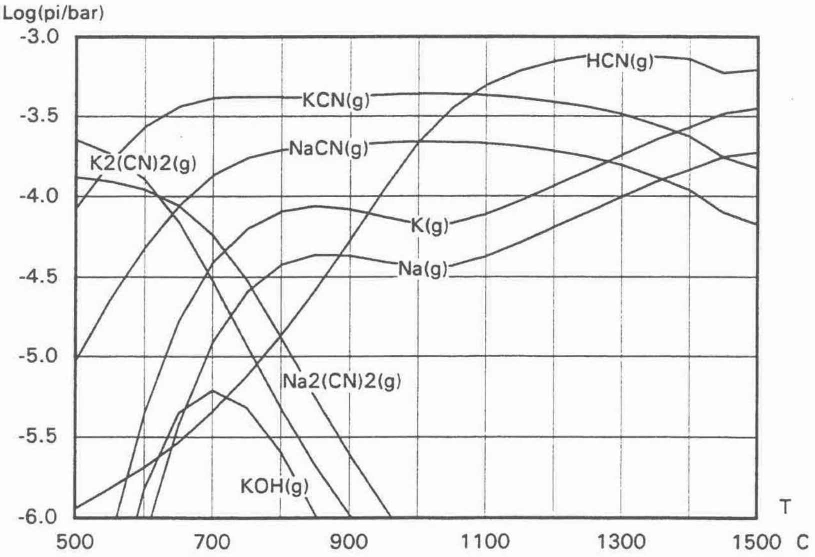

FIG.5. Composition of a metastable gas mixture obtained by cooling the equilibrium gas mixture from 2000 °C with restriction of carbon precipitation. Gas becomes increasingly oversaturated by carbon with decreasing temperature.

The total cyanide content in carbon saturated equilibrium gas calculated from partial pressures of cyanide species (Fig. 3) amounts to 110 and 53 mg CN /Nm^3 respectively, at 1300 °C and 800 °C. The corresponding total cyanide contents for the metastable, carbon oversaturated gas are one order of magnitude higher, 1379 and 721 mg CN /Nm^3 respectively. The former values fit well with the total cyanide contents, 50 mg/Nm^3 on average, measured in the furnace off-gas during the test period. These results might indicate that in spite of generally unfavourable kinetics of carbonaceous gaseous species decomposition with

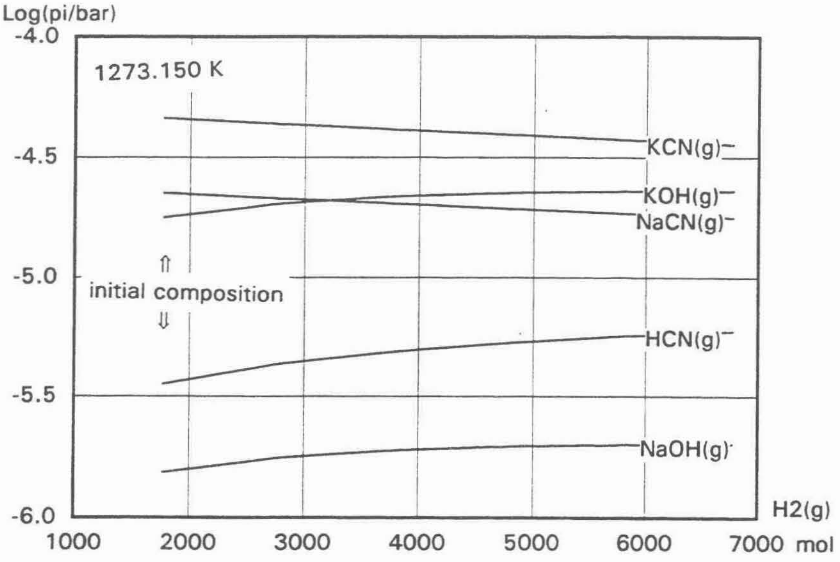

FIG. 6. Calculated effect of hydrogen additions on the equilibrium content of cyanides in carbon saturated gas at 1000 °C.

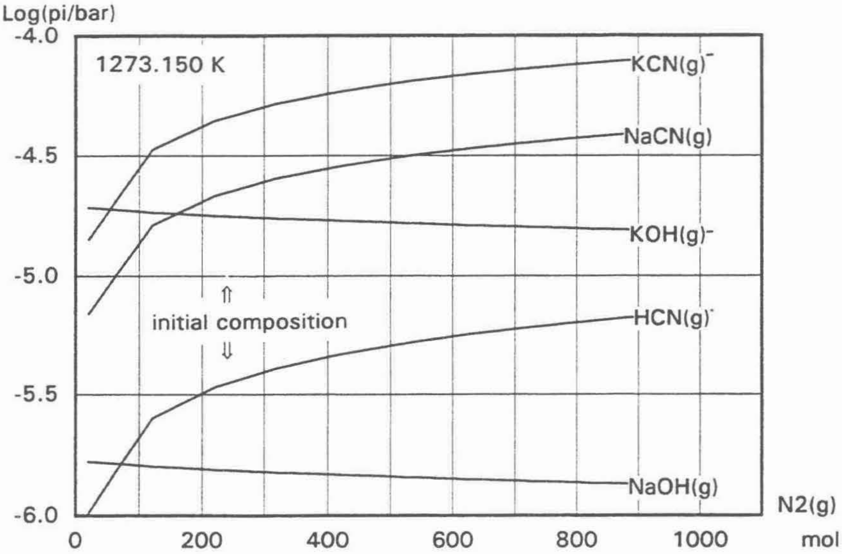

FIG. 7. Calculated effect of nitrogen additions on the equilibrium content of cyanides in carbon saturated gas at 1000 °C.

carbon precipitation, the furnace gases are close to the equilibrium with relation to carbon. Carbonaceous dust present in the furnace gas offers naturally a lot of favourable surface for heterogeneous nucleation for carbon. As the furnace gas is rapidly cooled down in the venturi scrubber, reactions tending to proceed beneath 800 °C will hardly have any kinetic prerequisites to advance and cyanide amounts present in the furnace gases can be expected to be found in the gas washing water.

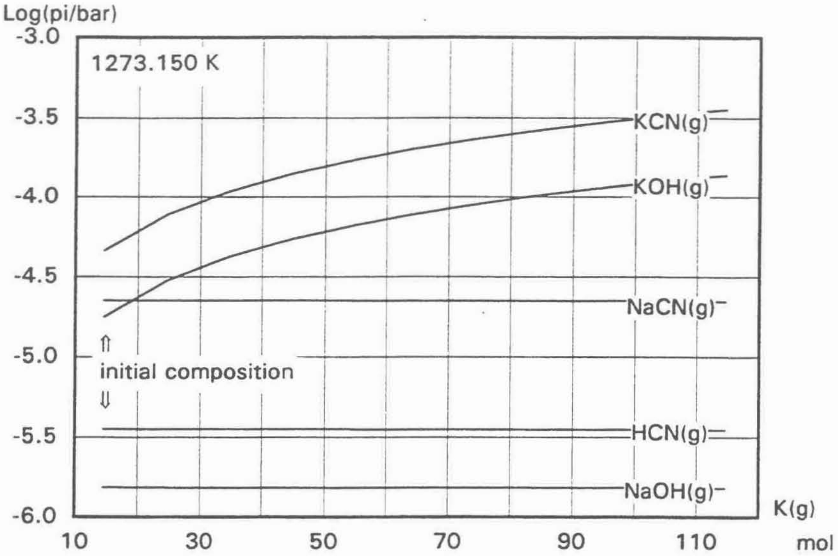

FIG. 8. Calculated effect of alkali (potassium) additions on the equilibrium content of cyanides in carbon saturated gas at 1000 °C.

PLANT AND LABORATORY TESTS

Plant tests for determination of cyanides in furnace gas and scrubbing water

The plant measurements were performed in Outokumpu Chrome's ferrochrome works at Tornio. Gas and water samples were gathered from the bigger ferrochrome furnace with an active power of 55 MW. The gas temperature was 800 °C. The samples were sucked from the gas atmosphere just above the burden, 1.3 - 2.4 m inside the furnace, between the electrodes. The samples were sucked through a dust filter and through absorption flasks where the cyanides were dissolved. Part of the gas was gathered in gas receivers for composition analysis. In addition to the gas samples from the furnace, samples after the venturi scrubbers also were taken. The aim of the gathered gas samples was to clarify the total cyanide content of the furnace gas, solubility of cyanides into the gas scrubbing waters and the SO_2, K, and Na contents. The equipment for gathering of gas samples is presented in Fig. 9.

The behaviour of cyanides in the slag granulation was examined using water samples before and after granulation. The removal mechanism of cyanides from the waters by vaporization and dissolution was also examined from the granulation vapours.

The cyanide contents were analyzed from the water solutions by cyanide activity electrochemical sensor, for which reason the disturbing sulphides were removed from the samples before measurement. For SO_2 samples a gravimetric measurement from H_2O_2 solutions was performed. K and Na contents were analyzed from water solutions by using an atom absorption spectrometer. Moisture of the gas was measured by H_2O absorption tube and the composition by gas chromatography. Dust collected in the dust filters was analyzed chemically. Alkalinity was measured from the scrubbing waters.

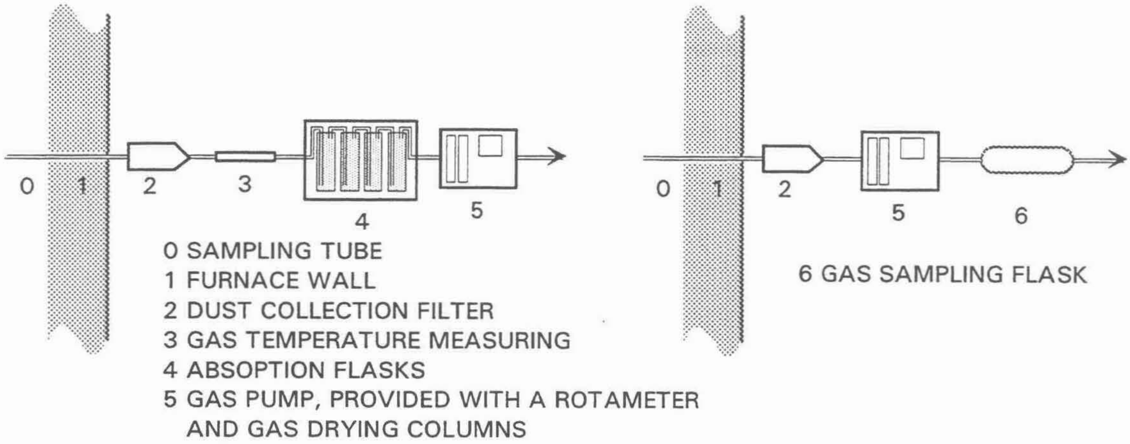

FIG. 9. Gas sampling equipment from the smelting furnace.

Results of plant tests

There were variations in the composition of the analyzed furnace gas, in general the CO content was $\geq$ 80 %. The total cyanide content in the furnace gas was on average 50 mg/Nm^3 of which the gaseous cyanides were 13 - 70 mg/Nm^3, on average 35 mg/Nm^3. The amount of dust in the gas was on average 16 g/Nm^3 and the cyanide content of the dust 0.005 - 0.29 %. This cyanide content was in relation to the potassium content in the dust. The sodium content was nearly constant. After the venturi scrubbers the cyanide content in the gas was $<$ 1 mg/Nm^3. The cyanides totally dissolved in the scrubbing waters. The measured cyanide contents correspond to apparent partial pressures of 10^{-4} to 10^{-5} bar for cyanide radical CN in the furnace atmosphere. The SO_2 content in the gas was $<$ 1 mg/Nm^3, sodium content was 160 mg/Nm^3 and potassium content 550 mg/Nm^3. Sodium and potassium were totally in the dust.

The scrubbing water is consciously used after clarifying in granulation. Its cyanide content was 7 - 12 mg/l and pH 8 - 9. In granulation the cyanide content of the water decreased to a level of 2 - 5 mg/l, i.e. the removal from the water was 70 %. The content decreased further in the settling ponds. At the end of the water circulation the cyanide content was $\leq$ 0.2 mg/l which is clearly below the permissible limits.

Analyzing of the water vapour from the granulation hood proved that up to 10 % of the removed cyanides go into water vapour and water droplets. The rest vaporizes directly as HCN, which oxidizes in the air very rapidly.

Laboratory experiments on the stabilization of gaseous cyanides by alkalies

The aim of the tests carried out at the Outokumpu Research laboratory in Pori was to confirm the effect of alkalies on the formation of gaseous cyanide species. Tests were performed by smelting a charge of chromite pellets with and without potassium feldspar addition in a covered Al_2O_3 crucible in an induction furnace.

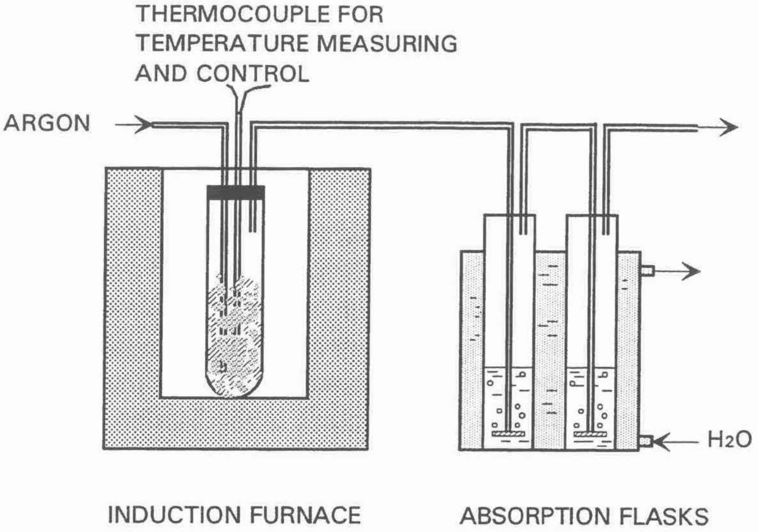

FIG. 10. Test arrangement for cyanide measurement.

The charge was heated up at a rate of 600 °C/hour to a temperature of 1650 °C under an argon flow of 0.3 dm^3/min. After ten minutes holding time at a temperature of 1650 °C, the charge was cooled down under argon flow. Gas from the furnace was washed in two gas absorption water flasks in series. The total CN^- content was analyzed as in the plant tests. The test arrangement is presented in Fig. 10.

In these tests coke was the only source of nitrogen. The atmosphere was very reducing. The results of the tests are shown in Table III.

TABLE III. The effect of feldspar addition on the cyanide formation.

Sample	Alkalies kg/t pellets	CN in gas mg/t pellets
Pellet	1.2	690
Pellet + feldspar	21.7	2870

An increase of alkali content in pellets from 1 kg to 22 kg per ton of pellets increases the cyanide content roughly fourfold in the argon flow. The results clearly confirmed the assumption that the presence of alkalies in the charge enhance the formation of gaseous alkali cyanides.

CONCLUSIONS

In the Outokumpu ferrochrome process smelting takes place in a totally closed submerged arc furnace. The formed CO-gas is not burned in the furnace but gathered from the furnace and utilized as fuel in the works. The conditions in the closed smelting furnace are too reducing for the formation of NO_x or chromium trioxide, but are favourable for cyanide formation.

Both thermodynamical calculations and measurements show that gaseous cyanides in the Tornio ferrochrome smelting furnace amount to a level of 30 - 70 mg/Nm^3 of furnace gas. These cyanides are transferred substantially into the venturi scrubber water. According to laboratory tests and equilibrium calculation, the cyanide level in the gas is mainly controlled by nitrogen and alkali contents of the charge. The smelting tests made in laboratory confirmed the strong effect of alkalies. The nitrogen present in the burden, offering a favourable environment for cyanide formation, originates at the Tornio smelter mainly from the coke, which has an exceptionally high nitrogen content due to the nitrogen quenching of hot coke. With a charge of high alkali and nitrogen content, cyanide formation in the furnace might cause problems without proper control of waste waters.

Measurements in practice show that the cyanides formed in the smelting furnace dissolve completely into the scrubbing water in furnace gas cleaning. The cyanides are unstable in water and the increase in temperature enhances the decomposition and vaporization.

The slag granulation of ferrochrome smelting offers good conditions for cyanide decomposition from the scrubbing water. The active factors are the increase of water temperature from 15 °C to 60 °C, effective mixing and suitable pH. The temperature of the slag coming into granulation is almost 1700 °C which causes intense vaporization of water. The importance of the increase in water temperature is emphasized during the cold winter time. The cyanide content in the scrubbing water was 7 - 12 mg/l, but was decreased in granulation to a level of 2 - 5 mg/l. The final oxidation takes place in the settling ponds. As a result, the cyanide content in the effluent was less than 0.2 mg/l, which is way under the permissible limits.

REFERENCES

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