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THE ECONOMIC AND TECHNICAL IMPLICATIONS OF THE USE OF COAL RATHER THAN COKE AS A REDUCTANT AT METALLOYS.

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ABSTRACT

Samancor's ferromanganese production facility at Meyerton consists of nine furnaces ranging from 9 to 81 MVA. Three of these furnaces (M10, M11 and M12) are large closed units producing combustible off gas. Coke is in short supply in South Africa; hence 70-80% of the carbon required for the reduction of the ore in M10, M11 and M12 is supplied in the form of coal. As these are closed furnaces, the volatiles from the coal are not burnt above the burden and leave the furnaces in the off gas. This volatile matter is scrubbed out in the wet scrubbers and is entrained and dissolved in the scrubber effluent. The scrubber effluent is then pumped into sealed settling dams where the solids and entrained organics settle out. The supernatant liquid containing the dissolved organics (mainly in the form of phenols) is returned to the scrubbers. A consequence of this closed circuit operation is that concentration of phenols build to values in excess of 1500ppm, which are above the legislated value of 5 ppm. This paper weighs up the economic advantages from the use of coal against the solutions to the problems mentioned above.

INTRODUCTION

Metalloys, which is Samancor's manganese alloy production facility, is situated at Meyerton, near Johannesburg, and operates nine furnaces. Of these, two are small (7,5 MVA) open units, four are intermediate (21 MVA) open units and three are large (75 - 81 MVA) closed furnaces. Generally, all the furnaces can be used interchangeably to produce either ferromanganese or silicomanganese from Samancor's ore from the Kalahari manganese field.

The gas emanating from the process contains high loadings of manganese which is removed prior to discharge of the gas to atmosphere. In the case of the small and medium furnaces, the gas is combusted above the furnace burden, then cleaned in conventional bag houses. In the case of the large closed production units, a combustible gas leaves the process, is cleaned in wet Venturi scrubbers and is then flared to atmosphere. In the future, this gas will be used to produce electricity.

Coke, which is used by most manganese alloy producers as the reductant in the production process, is in short supply in South Africa (due to the lack of coking coal reserves) and is consequently expensive. Good metallurgical grade coal is in relatively abundant supply in the country; hence is cheap and is used by Metalloys for 90% of the reductant requirements.

The use of coal rather than coke as a reductant provides Metalloys with a major economic advantage but does create some technical difficulties. These problems do not manifest themselves in the metallurgical operation of the furnaces, but cause a pollution problem in the effluent from the wet Venturi scrubbers as the volatile matter from the coal reports to these streams. This is not a problem in the small open furnaces as the volatiles are completely combusted above the burden in the furnaces and report to atmosphere as carbon dioxide. The purpose of this paper is to weigh these difficulties against the economic advantages mentioned above.

ECONOMIC CONSIDERATIONS

The comparative delivered prices of coal from Delmas Mine and coke from Iscor are given in table 1 below.

TABLE 1 - Comparative price of coal and coke.

	Delmas coal	Iscor coke
Delivered price per ton	R83,63	R376,30
Delivered price per ton carbon	R122,98	R453,37
Difference coke - coal per ton carbon	R330,30	

From the above difference in the price per ton of carbon and the usage of approximately 163 000 tons of carbon per annum, the use of coal rather than coke realises savings of R54 million per annum.

TECHNICAL CONSIDERATIONS

In the current operation, effluent from the wet scrubbers (which consists of suspended solids and water) is pumped to PVC lined penstock settling dams. The composition of the effluent is shown in table 2 and the effluent is circulated at 520m^3 per hour.

TABLE 2 - Composition of Scrubber Effluent

Analysis of dust				Analysis of Phenolic liquor	
	FeMn dust %	SiMn dust %			mg/l
Mn	36,4	22,4		COD	5000
Fe	1,5	0,6		Ammonia	750
CaO	4,0	3,1		Thiocyanate	320
MgO	3,3	3,7		Cyanide	12
SiO_2	4,2	27,6		Sulphates	490
Al_2O_3	2,0	2,2		Chlorides	525
C	26,1	25,4			

Here the solid material settles out together with the tars and oils and the supernatant liquid is pumped back to the scrubber circuits. The content of phenols in the liquor is order of magnitudes above current legal requirements. Once a dam has been filled with solids and been allowed to dry, spontaneous combustion of the solids occurs as a result of the high free carbon content of the solid material. This practice is obviously unacceptable in the face of increasing environmental awareness.

The above problem is aggravated by the geological instability of the dolomitic structures which underlie the dams. Ground subsidences are possible and, as a consequence, the integrity of the dam linings cannot be guaranteed. A process to replace the operation of the dams is therefore necessary to facilitate the ongoing use of coal in the process. A benefit would be gained from the process if the manganese containing solid material could be recovered in a form that would render it suitable to return to the furnaces. The development of this process is described in the following section.

DEVELOPMENT OF A SOLUTION

Three processing stages are envisaged for treatment of the effluent:

* Solids/liquid separation
* Solids recovery and beneficiation
* Phenolic degradation.

The flowsheet of a proposed process is shown in FIG.1 and the development of each unit process is described below.

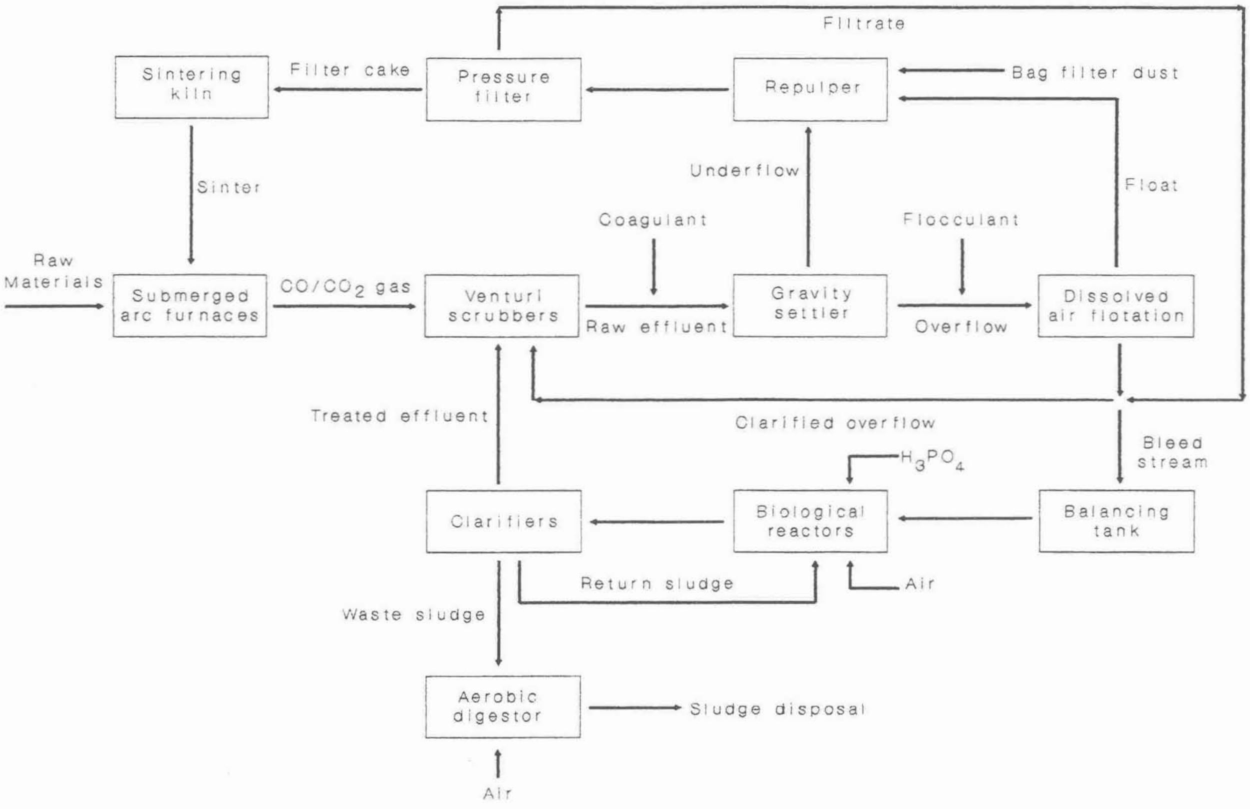

Fig 1. Block flow diagram of the proposed treatment plant.

Solids/Liquid Separation

Clarification in gravity thickeners, aided by addition of low concentrations of polyaluminium chloride co-polymer, ensures a Coe & Clevenger settling rate of 5.4m/hr and a 98% recovery of suspended solids. Solids are discharged from the thickener as a slurry containing 10% dry solids which is sent to filtration for the recovery of the solid matter.

The thickener overflow is further clarified by dissolved air flotation (DAF) aided by trace additions of acrylamide polymer. The final supernatant yields a total suspended solids concentration of less than 25 mg/l, and a reduction in total oils concentration from 120 mg/l, to less than 20 mg/l [2]. The phenol content of the liquor is unchanged in the process.

Solid liquid separation ensures a total 99.3% recovery of suspended solids [3].

Solids Recovery and Beneficiation

The thickener underflow, DAF float, and manganese bag filter dust originating from Samancor's smaller open furnaces operations, may be repulped to produce a homogeneous filter feed. The addition of bag filter dust to dry scrubber solids is based on an arising production ratio of 2:3.

Pressure filtration produces a 15mm cake of 23% residual moisture content. The filtration flux is approximately 65kg/m^2.h yielding a filtrate containing less than 50 mg/l of suspended solids [4].

Comparatively, pressure filtration produces a filter cake of lower transportable moisture content than most conventional vacuum filtration techniques, and thereby eliminates the likelihood of the product returning to its characteristic thixotropic state on handling.

The filter cake is a robust product which can be sent directly to a sintering kiln without further agglomeration. The cake contains approximately 20% free carbon and has a net calorific value of 7MJ/kg; hence, it exhibits the phenomenon of spontaneous ignition. Controlled combustion and sintering of the cake is therefore necessary before the cake can be stockpiled and recycled back to the gravity-choke fed furnaces.

Pilot studies determined that sintering requires preheating of the filter cake to approximately 250°C to drive off the excess moisture and commence ignition. Oxidation of the excess carbon by CO_2 and calcining of Mn-carbonate compounds takes place at 250°C - 650°C under an inert CO_2 atmosphere depleted of oxygen. Sintering of the silicon dust takes place at 1080°C and reduction of Mn-oxides proceeds gradually at 1150°C in an air-atmosphere [5].

The sinter is an extremely fine grained CaMn-silicate with the major phase present as bustamite ($CaMnSiO_3$) [6].

The CO_2 gas produced in the kiln is successfully utilized to dry the moist incoming filter cake, and provides for the atmospheric conditions required for calcining and oxidation of excess carbon.

The requirement for further wet scrubbing and thermal post combustion of kiln off gas is eliminated, as any polyaromatic hydrocarbons in the gas are completely oxidized in the counter current flow of the gas through the ignition and firing zones of the sinter hearth [7].

Phenolic Degradation

Testwork was undertaken to assess the viability of both carbon adsorption and biodegradation to remove phenols from the reticulating circuit. Extrapolation of the results obtained from activated carbon adsorption testwork indicated that both the high capital and operating costs and poor market value of phenol made this option unattractive.

This led to the decision to further investigate biological treatment at pilot scale.

The bio-oxidation process is a complex intracellular chain of reactions facilitated by enzymes (modified protein). Micro-organisms convert the contaminating components of effluent water into new bacterial cells and non-toxic (CO_2 and H_2O) components [8].

A general equation of the biological oxidation can be illustrated as follows:

$$\underset{\substack{\text{Organic}\\\text{Matter}}}{\text{COHNS}} + O_2 + \text{Nutrients} \rightarrow CO_2 + NH_3 + \underset{\substack{\text{New}\\\text{bacterial}\\\text{cells}}}{C_5H_2NO_3} + \text{Other end products}$$

$$\text{Phenol (COD)} + O_2 + \underline{\text{Pseudomonas}} \rightarrow CO_2 + H_2O + \underline{\text{Pseudomonas}}$$

Inclusion of the dissolved air flotation stage after gravity settlement and prior to biological treatment was imperative to reduce the oil concentrations to less than 20 mg/l in the feed to the biological reactors.

This finding is confirmed by the work of Galil and Alkhatib who reported poor settleability of sludge due to entrainment of hydrocarbons in biological flocs and the adverse effects on biological activity [9] [10].

Microscopic observations of activated sludge indicated good floc formation with no evidence of filamentous organisms. Free swimming and stalked ciliates were present, and settlement of sludge was readily maintained in the absence of oils, with SVI (Sludge Volume Index) values of between 80 - 90 ml/g.

Initially a single biological reactor was used but was replaced by a two stage system.

The operation of two stage reactors demonstrates many benefits when compared to quasi-plug flow or single stage reactors. Two stage bio-oxidation led to improved COD removal and a consistently high degradation of phenol. Hydraulic loading limitations and sporadic peak effluent phenol concentrations experienced in a single stage reactor could be overcome. Table 3 details a summary of results obtained from single and two stage biological reactors.

TABLE 3 - Comparison of the performance of single and two stage biodegradation.

		Single stage	Two stage	
Hydraulic Retention Time (hr)		40	16	10
COD (mg/l)	Influent average	2815	2270	749
	Range	870 - 5918	1550 - 7287	
	Effluent average	1015	749	415
	Reduction (%)	64	67	45
	Total Reduction (%)	64	82	
Phenol (mg/l	Influent average	621	416	42
	Range	168 - 3155	244 - 542	
	Effluent average	52	42	2
	Reduction (%)	89	90	95
	Total Reduction (%)	89	99.5	

The increased reduction of COD indicates that readily biodegradable organics are degraded in the first aeration tank and the less biodegradable compounds are than utilised in the second reactor. The net degradation efficiency increased to such a degree that periodically insufficient COD remained to sustain biological activity in the second reactor, and endogenous respiration caused a reduction in the active biomass concentration.

Of primary importance to the scale up of the plant is the reduced hydraulic retention time.

Nitrification of ammonia could not be promoted despite the addition of activated sludge taken from an actively nitrifying municipal plant, and dissolved oxygen concentrations of 2 mg/l. It has been concluded that the presence of phenol, cyanide and thiocyanate is detrimental to nitrification as these compounds are known to inhibit the nitrifying bacteria in a completely mixed reactor [11].

CAPITAL EVALUATION OF THE PLANT

The estimate of the capital required to establish the plant is given below.

Clarifiers/DAF	≈	R 2,0 million
Pressure filters	≈	R 4,0 million
Kiln	≈	R15,0 million
Materials handing	≈	R 4,0 million
Biological	≈	R20,0 million
	≈	R45,0 million

The alternative to meet environmental requirements would be to revert to the use of coke as a reductant which will cost an addition R54 million per annum. On this basis, there is therefore no alternative but to proceed with the project.

CONCLUSION

The use of coal as a reductant in ferromanganese production in South Africa provides economic benefits and is in the country's interests due to the limited reserves of coking coal. The use of coal does result in technical difficulties in general , and in particular with the treatment of scrubber effluent. A solution to these problems that is both technically and economically viable has been devised and will be implemented so that the use of coal will continue in spite of tighter environmental legislation.

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