THE POTENTIAL FOR THE DIRECT PRODUCTION OF FERROCHROMIUM NICKEL ALLOYS AND STAINLESS STEEL "PIG" IN ZIMBABWE

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(presented by Dr. Slatter)

SYNOPSIS

Weathering of the serpentinite in the north of the Great Dyke of Zimbabwe has produced concentrations of up to 2 % Ni. These are potential ore bodies but are difficult to benificiate because the Ni occurs in the silicate lattice. Tests have shown that this material can be smelted together with eluvial chromite concentrates from the overlying soil cover to produce a range of ferrochromium nickel alloys. As the proportion of nickel silicate in the charge increases, the Ni content of the alloys increases from approx. 3 % to 12 % and the Cr decreases from 52 % to 23 %. It is anticipated that the high-Cr, low-Ni alloys could be used as addition alloys similar to charge chrome for stainless steel production. Alloys with greater Ni and lower Cr contents could be used for heat-and corrosion-resistant cast irons and steel. Alloys which contain approx. 25 % Cr and 11 % Ni are referred to as stainless steel "pig" due to their relatively high contents of C and Si but they can be refined to stainless steels by decarburising. It is concluded that the production of ferrochromium nickel alloys by this process provides an interesting possibility for the exploitation of a unique combination of ores on the Great Dyke.

Introduction

The Great Dyke of Zimbabwe is a large, layered igneous intrusion of ultramafic rocks, mainly serpentinite and pyroxenite. It extends across Zimbabwe for approximately 500 km in an almost straight line from NNE to SSW and has a maximum surface width of approximately 10 km.

It is known best for its extremely large reserves of what were formerly known as metallurgical grade chromium ores but are better referred to now as high-chromium ores; i.e. ores containing 46 % or more Cr_2O_3 and with a Cr:Fe ratio exceeding 2:1. The chromite occurs generally in narrow seams which dip inwards from the flanks of the Dyke to the axis, but deposits of eluvial chromite occur also and these are referred to later.

In addition to chromium there are other potentially important metals associated with the Great Dyke. One example is the platinum-group metals

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for which the reserves are very large although the grade is lower than the ore which is mined in the geologically-related Bushveld Igneous Complex in South Africa.

Another metal of potential economic importance associated with the Great Dyke is nickel, which occurs enriched in weathered serpentinite as a silicate. In its fresh, unaltered state, the serpentinite contains nickel in small amounts with some chromium, although neither are in sufficient quantity to warrant any mining interest, Table 1.

Table 1 : Typical composition of fresh serpentinite from the Great Dyke.

component	wt. %
SiO_2	39,3
MgO	39,3
Al_2O_3	1,2
FeO	4,1
Cr_2O_3	3,1
NiO	0,12
l.o.i.	13,0

Under conditions of extreme weathering of the serpentinite, such as occur towards the northern end of the Great Dyke, the nickel tends to migrate downwards and it becomes concentrated in the weathered rock close to the interface with the fresh rock. This effect can produce concentrations of 1-2 % Ni, although even higher concentrations may occur locally, and these occurrences then assume some significance as potential nickel ore deposits. However, one of the problems associated with this type of deposit is that the nickel occurs within the silicate lattice and therefore the material cannot be beneficiated by gravity or magnetic separation or by flotation. Nevertheless, similar ores elsewhere have been exploited by leaching to remove the nickel, or be smelting to ferronickel (1-4).

In 1971, the Institute of Mining Research successfully produced ferronickel from this material by smelting in a 30 kVA submerged arc furnace. The power consumption was, however, extremely high owing to the low grade of the deposit investigated (< 1 % Ni) and it was concluded that exploitation of the deposits by this means was unlikely to be economic.

No further interest was displayed in the deposits until 1975 and this resulted mainly from investigations upon an eluvial chromite deposit in the northern section of the Great Dyke. Eluvial chromite is derived from the weathering of the serpentinite such that its chromite content remains in situ while the weathered material is removed. Eventually there is a large concentration of chromite in the soil cover and a very pure chromite concentrate can be produced by simple mechanical beneficiation.

Removal of the soil cover for the production of chromite concentrates exposes the weathered serpentinite which may have been enriched in nickel by the process already described and this material can be easily removed by a second, deeper cut with the earth-moving equipment.

The very close relationship of the chromite and nickeliferous serpentinite initiated the opinion that perhaps these two materials should be treated as a unit and not separately. If they could be smelted together, the very high grade of the chromite concentrates would partly counteract the low grade of the nickel silicate and thus the power consumption per tonne of alloy could be more favourable. In addition, a new class of ferroalloys would result containing both chromium and nickel which might be useful for a variety of purposes.

Materials and procedure

On the recommendation of one of the mining companies in Zimbabwe, sampling traverses were made over an area where the eluvial chromite had already been removed, thus exposing the weathered serpentinite. The samples were found to contain 0,5 - 2,5 % Ni, although nickel contents were generally $>$ 1,2 %. On one of the traverses, approximately 2 % Ni occurred over more than 100 m. A one tonne bulk sample was collected from this zone for smelting trials, together with eluvial chromite concentrates from the same area. The compositions of both these materials are given in Table 2.

It is evident that the nickeliferous material is a hydrated magnesium-iron silicate containing approximately 2 % Ni and some chromite. The chromite concentrate has a high content of Cr_2O_3, although its Cr:Fe ratio is only 2,4:1 due to a relatively high content of FeO.

Table 2 Composition of nickel silicate and eluvial chromite concentrate.

component (wt. %)	nickel silicate	chromite concentrate
NiO	2,57	-
Cr_2O_3	1,5	53,8
FeO	7,6	19,8
SiO_2	40,3	5,5
Al_2O_3	0,5	13,8
MgO	29,0	7,0
CaO	0,8	0,2
l.o.i.	15,5	-

Test smelting was carried out in 72 kVA submerged arc furnace using mixed charges of nickel silicate to chromite concentrate in proportions ranging from 1:1 to 10:1. Wankie coke was used as the reductant.

In order to compare the power requirements and smelting conditions, each test smelt was carried out according to a strictly standardised procedure. This included precise sizing of the charge, addition of the charge at a fixed rate, and operation of the furnace at a fixed voltage and within a controlled current range. The same conditions had been used for the production of high-carbon ferrochromium from a standard charge used by an industrial producer, giving a factor of 0,422 to convert the power requirements for batch smelting in the 72 kVA furnace to that for continuous smelting in an 18 MVA furnace.

Calculations of the theoretical compositions, liquidus temperatures and basicities of the slags which would result from smelting the various mixtures of nickel silicate and chromite concentrate indicated that it would probably not be necessary to incorporate additional fluxes in the charge; an extremely important factor in relation to the power consumption for the smelts.

Composition of charges and smelting results

The average composition of the test charges and the results of the smelts are given in Table 3.

Table 3 Compositions of charges and smelting results from tests to produce ferrochromium nickel alloys*

nickel silicate : chromite concentrate	charge composition (wt %)			smelt performance		
	nickel silicate	chromite concentrate	coke	time (min)	power (kwh)	tapping temp. (°C)
1:1	43,1	43,1	13,8	92	54,6	1700
2:1	59,6	29,8	10,6	93	55,3	1670
4:1	73,7	18,5	7,8	84	51,0	1660
6:1	79,9	13,3	6,8	85	51,6	1700
8:1	83,4	10,4	6,2	74	50,1	1680
10:1	86,0	8,6	5,4	69	47,3	1710

* 30 kg charges

From Table 3, it is evident that as the proportion of nickel silicate in the charge increases, smelting times and total power consumption decrease for a fixed charge weight. Tapping temperatures varied between 1660° C. and

1720^{o} C. and there was little evidence of slag attack on the magnesite furnace lining.

The average yields of alloy and slag and the rate of alloy production are summarised in Table 4 and compared with similar figures for the production of high-carbon ferrochromium in the same furnace and under the same operating conditions.

Table 4 Average yields of alloy and slag and rate of alloy production*.

nickel silicate : chromite concentrate	average yields (kg)		rate of alloy production (kg/h)
	alloy	slag	
1:1	6,5	12,0	4,3
2:1	5,6	14,7	3,6
4:1	4,5	16,5	3,2
6:1	3,9	17,2	2,8
8:1	3,2	18,7	2,6
10:1	3,0	19,3	2,6
high-carbon ferrochromium	6,2	13,9	4,1

* 30 kg charges

From Table 4, the 1:1 charge has an alloy yield similar to that of high-carbon ferrochromium but this decreases to less than half for the 10:1 charge. The rate of alloy production does not, however, decrease at the same rate because charges with larger proportions of nickel silicate have shorter smelting times (see Table 3). Thus, although the alloy yield from the 10:1 charge is only 48 % of that from the high-carbon ferrochromium charge, the rate of alloy production is 63 % of the high-carbon ferrochromium rate.

The average slag yield from the 1:1 charge is slightly less than that of high-carbon ferrochromium, but this increases by approximately 60 % for the 10:1 charge.

Slag compositions

The average compositions of the slags and their theoretical liquidus temperatures and basicities are given in Table 5 and compared with those for high-carbon ferrochromium.

Table 5 Average compositions of slags from the production of ferrochromium nickel alloys and their theoretical liquidus temperatures and basicities.

nickel silicate : chromite concentrate	average slag compositions (wt%)						liquidus temp. (° C.)	basicity
	SiO_2	MgO	Al_2O_3	CaO	Cr_2O_3	FeO		
1:1	38,8	37,3	16,9	0,2	4,0	1,0	1680	0,97
2:1	46,0	38,1	11,2	0,3	2,6	0,8	1660	0,83
4:1	47,5	45,1	5,4	0,2	2,6	1,2	1740	0,95
6:1	47,9	46,6	4,0	0,2	1,7	1,3	1780	0,98
8:1	49,8	43,8	2,9	0,2	2,1	1,5	1720	0,88
10:1	49,5	44,2	2,7	0,2	2,6	1,7	1730	0,90
high-carbon ferrochromium	35,4	30,2	26,1	3,9	3,4	0,9	1750	0,96

It is evident that the slags are higher in SiO_2 and MgO, and lower in Al_2O_3 than the ferrochromium slag. The theoretical liquidus temperatures are, however, similar to the ferrochromium slag, or even lower, and the basicities are also very similar. MgO and SiO_2 both tend to increase and Al_2O_3 shows a marked decrease as the proportion of nickel silicate in the charge increases. The simultaneous increase in MgO as SiO_2 increases tends to balance the basicity of the slag. Similarly the electrical resistivity of the slag tends to be balanced, for although MgO decreases the resistivity, SiO_2 has the opposite effect.

Alloy composition

The average compositions of the alloys from the smelts are given in Table 6.

Table 6 Average compositions of alloys from smelting mixed charges of nickel silicate and chromite concentrate.

nickel silicate : chromite concentrate	average alloy composition (wt.%)						
	Cr	Ni	C	Si	Mn	S	P
1:1	51,8	3,3	7,8	0,25	0,2	0,05	0,04
2:1	46,2	5,6	7,2	0,40	0,2	0,04	0,03
4:1	39,7	8,2	6,4	2,5	0,2	0,04	0,02
6:1	31,2	10,7	5,3	3,9	0,2	0,03	0,03
8:1	27,8	11,7	5,1	3,7	0,2	0,03	0,03
10:1	23,3	12,1	5,0	2,5	0,2	0,03	0,03
high-carbon ferrochromium	68,5	-	5,7	1,2	0,2	0,05	0,02

The composition is controlled by the chromium, iron and nickel contents of the two ores, by the relative proportions of the ores in the charge and by the amount of reductant in the charge. The reductant should exceed the stoichimetric requirements, but the amount by which it does so is somewhat critical; too little results in poor recoveries of chromium and nickel, whereas too much results in an excessively high silicon content in the alloy.

The greater activity, or concentration, of SiO_2 in the charges containing larger proportions of nickel silicate make it necessary to accept higher silicon contents in the alloy in order to achieve reasonable metal recoveries. Thus, although alloys from the 1:1 charges may have < 0,5 % Si, alloys from the 8:1 and 10:1 charges are not likely to contain < 2-3 % Si.

The decrease in chromium content and increase in nickel content of the alloy as the proportion of nickel silicate in the charge increases is evident in Table 6. There is a simultaneous decrease in carbon content from 7,8 % to 5,0 % resulting from the decrease in the chromium, and thus the carbide, content of the alloys.

Recoveries of chromium and nickel

Recoveries of chromium in the alloy were generally somewhat low, from 70-80 % in the 1:1 to 6:1 charges, dropping to 60-70 % in the 8:1 charges. The low recoveries are partly due to the addition of the chromite as a fine concentrate in the charge. Recoveries would be improved by agglomerating the concentrates into pellets or briquettes. Agglomeration would probably be necessary anyway in industrial production in order to avoid blanketing of the charge in the submerged arc furnace.

Recoveries of nickel also decrease as the proportion of nickel silicate in the charge increases, from 80-90 % recovery in the 1:1 to 6:1 mixtures to

70-80 % recovery in the 8:1 and 10:1 mixtures.

Power requirements

The power requirements per tonne have been determined for the alloys and converted to the equivalent requirements for an 18 MVA plant furnace using the conversion factor of 0,422 established for the 72 kVA furnace, Table 7.

Table 7 Power requirements for ferrochromium nickel alloy production

nickel silicate : chromite concentrate	power, kwh/tonne of alloy	
	72 kVA furnace	18 MVA furnace
1:1	8390	3540
2:1	9970	4210
4:1	11390	4810
6:1	13395	5650
8:1	15675	6620
10:1	15770	6660
high-carbon ferrochromium	9480	4000

It is significant that the power required to produce one tonne of ferrochromium nickel from the 1:1 charge is approximately 12 % less than that for the high-carbon ferrochromium. This is due mainly to the somewhat lower smelting temperatures (1650-1700° C. as compared with 1750° C. for the ferrochromium) and to the more efficient smelting of the chromium ore as a fine-grained or agglomerated concentrate, rather than as a lump ore.

As the proportion of nickel silicate increases in the charge, the power requirements per tonne of alloy increase due to the increasing gangue content of the charge. For the 10:1 charge, the power requirements are approximately 65 % more than for high-carbon ferrochromium.

Potential uses of the alloys

The wide range in composition of the alloys gives them a variety of potential uses, Table 8.

Table 8 Approximate compositions and related potential uses of ferrochromium nickel alloys

nickel silicate : chromite concentrate	approx. comp (wt.%)			potential use	
	Cr	Ni	C		
1:1	52	3,5	8,0	FeCrNi addition alloys	
2:1	46	5,5	7,0		
4:1	40	8,0	6,5	production of heat- and corrosion-resistant cast irons and steels	
6:1	31	10,5	5,5		
8:1	28	11,5	5,0		production of stainless steels
10:1	23	12,0	5,0		

Alloys produced from the 1:1 and 2:1 charges, containing up to 5,5 % Ni, are considered likely to be useful as addition alloys for the production of stainless steel. They would be used in the same manner as charge chrome, with the added advantage that some nickel is supplied with the chromium. The alloys are brittle and can be crushed to lump sizes for sale in the same manner as charge chrome or high-carbon ferrochromium.

Alloys produced from charges with 4:1 or more nickel silicate : chromite concentrate should be suitable for the production of heat- and corrosion-resistant cast irons and steels within the composition range 20-35 % Cr and up to 12 % Ni. For the cast irons, the carbon content should be 1 % - 4 % and therefore some decarburising of the alloys is required. At high carbon levels such as these, however, the removal of carbon can be easily accomplished by oxygen blowing of the molten alloy directly after tapping from the furnace, without incurring excessive loss of chromium.

The steels require carbon contents of less than 0,5 % and in this case the incorporation of argon with the oxygen will probably be necessary at an advanced stage of decarburisation in order to reduce chromium losses.

The production of iron and steel castings in this manner raises the interesting possibility of the foundry departing from its traditional defined role of melting and casting, to undertaking a full smelting operation of the raw ores followed by oxygen or argon-oxygen refining of the molten alloys and direct casting of the finished product. This would appear to have an economic advantage over the established method of producing these alloys which involve three separate components; the primary iron or steel, the chromium which is added as ferrochromium and the nickel which is added as pure nickel or ferronickel. Each of these three components has undergone a separate and costly production process during which time they have all been molten and then allowed to cool before being finally remelted together to produce the required alloy. This involves a large use and waste of heat which is energy which is costly.

Alloys produced from the 8:1 and 10:1 mixtures are suitable also for the production of austenitic stainless steels containing 18-20 % Cr and 8-12 % Ni.

The alloys may be marketed in ingots as stainless steel "pig" for subsequent remelting and refining to stainless steel or they may be tapped directly from the furnace into a converter for argon-oxygen refining. The alloys contain slightly more chromium than is required in the finished stainless steel and some chromium loss can, therefore, be accepted.

Value of the alloys

The most straight forward way of determining the potential value of the alloys is based upon their contents of chromium and nickel. For example, from the prices ruling for high-carbon ferrochromium and ferronickel in June 1980 (5) the calculated values are given and compared with high-carbon ferrochromium, Table 9. The values of the alloys increase as the amount of nickel increases, despite the simultaneous decrease in the amount of chromium, and reach a maximum for the alloy containing approximately 28 % Cr and 11,5 % Ni produced from the 8:1 mixture. The value of this alloy exceeds the high carbon ferrochromium by £ 141 / tonne, an increase of 37 %. The greater power consumption required for the alloy (see Table 7) would increase power costs by the equivalent of £ 10 in Zimbabwe, at the present contract power cost of 0,6 cents Zimbabwean/kwh.

Table 9 Calculated values of ferrochromium nickel alloys in June 1980 compared with high-carbon ferrochromium

nickel silicate : chromite concentrate	alloy composition (wt. %)		value in £ / tonne (US $ / tonne)		
n	Cr	Ni	Cr content	Ni content	total
1:1	52	3,5	295(699)	112(265)	407(964)
2:1	46	5,5	261(619)	175(415)	436(1034)
4:1	40	8,0	227(538)	255(604)	482(1142)
6:1	31	10,5	176(417)	335(794)	511(1211)
8:1	28	11,5	159(377)	367(870)	526(1246)
10:1	23	12,0	130(308)	383(908)	513(1216)
high-carbon ferrochromium	68	-	385(912)	-	385(912)

The calculated values of the alloys reflect only their contents of chromium and nickel. Their intrinsic values may well be greater for the reasons mentioned earlier relating to the inherent energy saving in alloys produced from a single smelting and refining cycle.

Apart from the energy savings aspect, there is a strong argument in favour of refining the stainless steel "pig" in the producer country immediately after tapping from the furnace, for this increases substantially the value of the product. For example, the price quoted by the British Steel Corporation in May 1980 for Series 304 stainless steel billets was £ 887 / tonne (6), an increase of 70 % over the theoretical value of £ 526 / tonne for the unrefined "pig".

Conclusions

The results of this test work have established the technical feasibility of producing a range of ferrochromium nickel alloys by directly smelting mixed charges of nickel silicate ores, from the weathering of nickeliferous serpentinite, and chromite concentrates. The alloys may be used for a variety of purposes depending upon their chromium and nickel contents, and these range from simple addition alloys for stainless steel production to alloys suitable for the production of heat- and corrosion-resistant cast irons and steels, and to alloys referred to as stainless steel "pig" which are suitable for refining directly to austenitic stainless steels.

The next important step is to investigate more thoroughly the potential nickel silicate ore reserves in order to establish whether these are sufficient to warrant large-scale exploitation and to determine their grade and variability. Favourable results would be followed by pilot-plant testing and in-depth surveys to determine the overall economics of the process.

In conclusion, although the commercial production of ferrochromium nickel alloys by direct smelting is not likely to take place in the near future, it is considered that the concept does hold promise for the successful exploitation of a unique combination of mineral resources on the Great Dyke of Zimbabwe.

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DISCUSSION

Dr. C. Finn[*]

The research is still very interesting and still very topical. I would like to ask one question with respect to Table 5 in which you gave the slag composition of smelting. You gave no value for nickel oxyde content in the slag. Does this imply 100% nickel recovery because, based on a rough mass balance for the 10:1 smelting case, it would appear that the nickel recovery is approximately 70%. Would you comment please?

Dr. D. Slatter:

I have recoveries of chromium nickel in the paper. I did not go into them as I was a bit short on time. But you are perfectly correct. In fact in a 1:1 mixture we were getting about 80 to 90% recovery of nickel and this dropped to about 70% in the 8:1 and 10:1 mixtures.

We could increase that recovery by increasing our reductant proportion to an extent, but then we are faced with the problem of a high silicon content reporting to the alloy. But I must say that I am sure that improvements could be made in the whole smelting process by perhaps changing the relative sizing of the reductant in the charge. Perhaps a finer reductant in the charge would improve the recovery. I think that there is ample room for further work in that field.

Mr. M. Sciarone[**]

I would like to ask about the silicious nickel ore. What is the approximate sizing? You said that the physical appearance, as well as the chemical composition is important. Would you mind telling us what is the size of materials?

Dr. D. Slatter:

The sizing of the ore was strictly controlled when we were charging to the furnace. As far as I remember, it was about minus 25 mm plus 12 mm. The ore itself, of course, comes out in big blocks, but weathered, and I think that what one would probably do in a production process is mill the ore, mix it with the chromite concentrates and pelletize or briquette it, and run it perhaps through a pre-heating rotary kiln to dehydrate it before charging to the furnace. The ore contains about 15% H_2O.

Mr. M. Sciarone

I was just going to suggest that the problem is with your chromite ore. It's too high in MgO. If you take some South African ore you can just mix it and you can use your nickel silicious ore just as a flux to the material. If you look at your metal you make with the high nickel content and the low chromium content, I think it is about time to charge the people for the iron which is in the metal.

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Dr. H. Knahl*

A question with regard to the transferability from your small pilot furnace of 72 KVA into a larger furnace scale. Have you planned for the future any trials in a larger scale or would you continue to run trials in a laboratory scale?

Dr. D. Slatter:

I think we would have to run trials to a larger scale, but I think the next step is to look more carefully at the ore reserves. Having established this, we would have to run trials on a larger scale perhaps about 0.5 MW. Perhaps we could make arrangements with the National Institute for Metallurgy and FAPA in South Africa to collaborate on that sort of programme because they have a suitable furnace for this. I think that is what would have to happen next. I might say that a plant operating on this sort of system could be either a metallurgist's delight or a metallurgist's nightmare depending on how one looks at it, because it would take very careful quality control of the two ore components in order to produce an exact composition. One would probably have a chromite concentrate which is constant in composition, but you might not be so lucky with the nickel ore whose composition may tend to vary and therefore the chemical balance would have to be very carefully controlled to make sure that you are getting the right proportions at all times in order to get the correct composition of alloy at the other end.

Mr. D.A.A. Reeves

I thought perhaps as the only steelmaker here I would make a comment. I think the pricing comments relative to the BSC 304 List Price are grossly misleading. You are comparing a stainless billet price with a raw material alloy price. Further, I think if I read the report correctly, all you are doing there is describing the effective price for the iron-chromium-nickel alloy, based on the nickel and chrome alloy prices ex Metal Bulletin and not a true production cost and price for your mixed alloy. And really the answer to whether these materials are going to be attractive to the steelmaker or not, will be dictated by the final price you are going to ask for this type of alloy.

Developing this a little, I think that not just odd alloys but the whole range of alloys you have indicated can be used in stainless steelmaking when using the arc-AOD route and, in fact, there could be a danger in your trying to be too sophisticated in tailoring chrome nickel ratios to particular markets. You must recognise that there is a whole family of stainless steels containing 12-25% chromium and varying from 7% nickel through to 20% nickel and you will be lucky if you get a particular alloy analysis to be tailor made and particularly suitable for the wide range of steels.

I would like to make a further comment about the carbon content of your alloys. With an AOD vessel I believe we can work the carbon out during steelmaking more cheaply than you can process it down to a lower carbon level by your normal alloy production methods and so, as a steelmaker, I would not be particularly worried, either about the carbon or the silicon contents you describe. In considering stainless steelmaking in Rhodesia using the mixed alloy,

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you will have to consider whether you can put down the size of plant in Rhodesia to make stainless steel, which would give the other economies of scale, which in Europe and elsewhere I feel counterbalance the economies of operations you may have based on using the mixed alloy.

At the end of the day, the attractiveness of the alloys you have described, really comes down to the real cost of the chrome and nickel units in the mixed alloy you generate, compared with the cost other producers elsewhere in the world produce the separate nickel alloys and chrome alloys, probably more efficiently. So for the steelmaker it will be still a comparison of the worth of this material to us at whatever level you decide to price it, compared with the price of a mixture of separate chrome and nickel and iron alloys from other suppliers.

Dr. D. Slatter:

I take your point certainly about the fact that you might find it easier to remove the carbon yourself than to do it at the source and as I say I find your comment very valuable and really it was the sort of reaction I was looking for. Thank you.