

RESEARCH AND DEVELOPMENT IN THE STEEL INDUSTRY IN NOVA SCOTIA *

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The world state of the art in ironmaking and steelmaking is examined, and an attempt is made to show where the present and future operations of the Sydney Steel Corp. fit into this world picture. Financial and political considerations are excluded from this examination. Examples are given of applied industrial and laboratory scale experiments, as well as fundamental investigations on chemical reactions important in steelmaking.

Introduction

Any attempt by one who is not employed in the industry to write authoritatively about it should be accompanied by some statement of one's bona fides. At the Atlantic Research Laboratory of the National Research Council we have been involved for 25 years in research on high temperature chemical reactions important in steelmaking. We have maintained close contact with developments at the Sydney Steel Corporation (SYSCO) and thus are generally familiar with the overall picture. We are part of the Atlantic Group for Research in Industrial Metallurgy (AGRIM), a cooperating group of metallurgical engineers and scientists at the Technical University of Nova Scotia, Nova Scotia Research Foundation Corporation, Dalhousie University, College of Cape Breton, the Cape Breton Development Corporation, and SYSCO. Some of the work which I will describe was sponsored by this group.

I intend to restrict this paper to aspects of steel production, and in order to define this more closely let me mention a few things I am not going to discuss. First of all I am not going to touch on the technology of steel fabrication, although it is obvious that our modern society will continue to benefit from research and development of new alloys for special applications. Very high strength steels, with the subsequent reduction in weight that they allow, are becoming more important. They bring with them serious problems such as fatigue failure and stress corrosion failure. Therefore research on heat-treating, machining, welding, corrosion, strength, etc., is being done all over the world in the fields of physical metallurgy, mechanical engineering, metal physics, and others. Such research may well be very important to Nova Scotia if we become, as some predict, technically sophisticated in such areas as ocean engineering. The Nova Scotia Research Foundation and Technical University of Nova Scotia are examples of local research institutes with clear interests in such areas. However, I suggest that the industry with which such efforts are related is manufacturing, rather than the basic steel industry, and so I will not discuss them further.

Really, what we are left with to discuss is SYSCO as the present basic industry, and investigations into the extractive metallurgy of iron and steelmaking as the research. Of course, we all know that economic and political implications underlie the technological side of this industry in Nova Scotia. It seems fairly obvious that even a technologically modern steel plant would find it difficult to turn a profit

under the burden of debt now attached to SYSCO, and so the continued existence of SYSCO appears to require favorable political decisions. In such a situation, for example, it could well be that a substantial effort should be devoted to research into various political methods of reducing SYSCO's capital debt load; this might pay better dividends than research into better ways of making steel. However, we must attempt here to stay away from such considerations. There are a number of papers on the economics of the industry, many in connection with the late CANSTEEL project, and one such background paper that can be recommended is titled "Steelmaking in the Atlantic Provinces" (1974). It was prepared by Atlantic Provinces Economic Council in 1974 and still is relevant.

My paper, then, is about the technology of steelmaking, and it is in 2 parts. The first is an examination of the world state of the art in ironmaking and steelmaking, with an attempt to show where the present and future SYSCO operation fits. The second is a look at some current local research, including industrial scale programs and fundamental laboratory studies.

World Steel Production

In 1978 world steel production was about 540,000,000 tonnes, with roughly 25% contributed by each of western Europe, eastern Europe plus USSR, North America, and Asia. In total, the western world produces 66% of the world's steel. Canada makes a considerable contribution, 2.1% in 1978, up from the 1.9% of 10 years ago. In 1980, when the current round of expansion of STELCO, DOFASCO and ALGOMA is finished, Canada's percentage will be approaching 3%. The 1978 production amounts to some 11,000,000 tonnes of steel and of this Nova Scotia makes between 0.5 and 1 million tonnes. Thus Nova Scotia makes between 0.1 and 0.2% of the world's steel.

To put the world's steel production in a somewhat more scientific context, we may calculate that the rate of production of new iron (not counting recycled scrap) is about 2.4×10^5 moles/sec. This is a very large number when we realize that laboratory experiments are usually on the scale of millimoles or micromoles per second.

The production of steel is a basic indicator of the industrialization of a country, and is often a source of national pride. Table I shows the per capita steel production

Table I. Per capita production of steel for selected countries

Country	Tonnes per capita*
Luxemburg	14.2
Belgium, Czechoslovakia, Japan	1.3-1.0
Canada, W. Germany, United States, USSR, Poland, Austria	0.7-0.6
Sweden, Italy, France, United Kingdom, E. Germany	0.5-0.4
Taiwan, Korea	0.2
China, India	0.04-0.02

*Steel production is for 1978, populations are for 1971.

of some arbitrarily chosen countries. Canada places well up among industrialized countries and in 1980 might rank with Japan. It is interesting to note that a plant of the size of SYSCO just about maintains the Atlantic provinces in line with the 0.5 - 0.7 tonnes/person/year figure.

Let us examine the technological state of the art. The overall process essentially is comprised of two steps: (1) ironmaking, followed by (2) steelmaking. Ironmaking is the reduction of iron ore, largely Fe_2O_3 , to a solid or liquid metallized product which contains 5 or 6% of impurities of one sort or another. Steelmaking is refining this crude product into a material of the correct chemical and physical properties to meet a customer's specifications. We do not make as much new iron as the steel production figures would indicate because of the recycling of scrap.

Ironmaking

Blast Furnace

Over 95% of the world's iron is produced in blast furnaces. These are tall stack furnaces where solids (ore, coke, and limestone) are put in at the top and liquids are taken out at the bottom on a more or less continuous basis. Figure 1 shows a typical configuration. Pre-heated air is forced in at the bottom and converts coke to CO , the heat of the reaction raising the temperature to 1500°C at which temperature CO can reduce the oxide to iron. Impurities in the ore, largely silicon, are combined with limestone as they are liberated to form a liquid slag. The characteristics of blast fur-

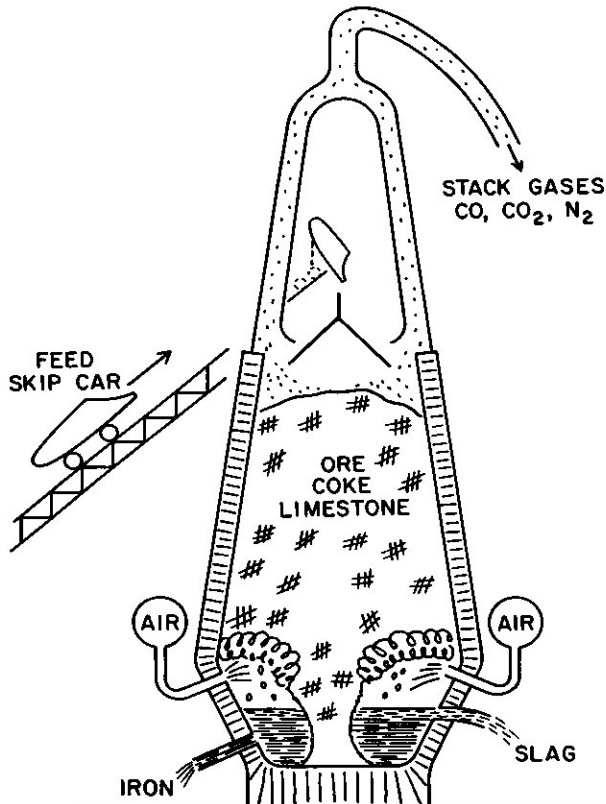


Fig 1 Configuration of typical blast furnace; 80 m high overall.

naces which have enabled them to compete successfully over the years are that they work by gravity, have a high throughput, and have no complicated machinery in the reaction zone. They conserve energy very well, and can be engineered to go on and on without interruption for several years. Actual chemical reactions take place in the center of the descending mass and away from the walls. All these advantages are improved by increased size, so that it is not surprising that their evolution has been in this direction.

The largest furnaces today are in Japan. A large furnace built recently by Bethlehem Steel in the United States may be taken as an example of modern furnaces. It has an inside hearth diameter of 13.6 m, and an interior working volume equivalent to 12 or so good sized houses. It can produce 8000 tonnes of iron a day! It is equipped with several hundred sensors for temperature, pressure, flow rate, etc., and is computer controlled. It cost \$200 million to build in 1977. The steady operation of expensive equipment like this must be ensured, and so the quality and regularity of feed materials must be closely controlled. No longer can random sized lumps of ore be fed. Modern feedstock typically would be about 50% pellets of pre-concentrated, well-sized ore and 50% sinter of ore and limestone. The object is to ensure a permeable bed of solids so that gas-solid chemical reactions can proceed efficiently. Coke must be of high quality, porous yet strong. The main cost incentive is to reduce the coke-rate, the number of kilograms of coke required to produce 1 tonne of liquid iron. In modern large furnaces this can be reduced to about 400 kg/tonne, with the help of about 75 kg/tonne of heavy oil or tar blown in with the air supply. Not only is the coke the single most expensive feed, but as it is essentially the sole source of the sulfur, keeping the coke-rate down reduces the sulfur problem. Table II is a comparison of old and new blast furnace technology.

Table II. Comparison of blast furnaces

	State of art in 1950		State of art in 1980	
		U.S. Steel No. 8	Bethlehem Steel "L"	Oita No. 2 Japan
Diameter (m)	9.5	9.8	13.6	15
Volume (m ³)	1275	2500	3700	5000
Tonnes/day	1470	4500	8000	12000
Tonnes/day/m ³	1.2	1.8	2.2	2.4
Coke rate kg/tonne	800	545	443	409

The smallest of the modern blast furnaces listed will produce about 1.6 million tonnes of hot metal a year and this, with scrap, will result in perhaps 2.5 million tonnes of steel. The present operations at SYSCO are in the 0.75 to 1 million tonnes/year range, and are provided by 2 relatively old furnaces which each produce about 800 tonnes/day. The coke rate can be 680/kg tonne, although this depends on the amount of limestone that must be added to take care of the sulfur. Thus the iron that they make is relatively expensive. The economy of size of 1 very large furnace is

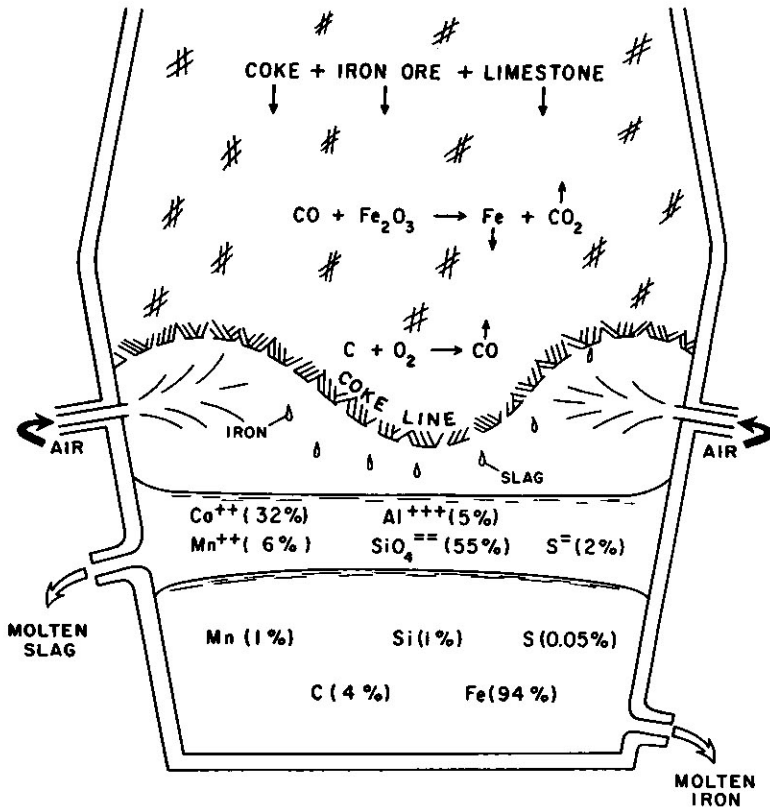


Fig 2 Chemistry of blast furnace.

just not applicable to the present SYSCO situation, although it would have been correct for the proposed CANSTEEL operation.

Before we leave the blast furnace, let us examine its chemistry in a simple manner (Fig 2). In the hearth of the blast furnace a metallic solution is in contact with an ionic solution, and is in more or less thermodynamic equilibrium with it and the gas phase, the latter setting the oxidation potential of the system at a very low level. The values given for the concentration of the various species (in weight percent) in the 2 solutions are merely typical of blast furnace operation. There has been much research over the years on all aspects of this equilibrium, and it continues today. For example, could we push this equilibrium in some desired direction by the judicious application of an EMF? The most troublesome impurity in the liquid iron is sulfur, and this comes almost entirely from the coke. Its elimination has been the subject of a study by AGRIM, as mentioned later.

Direct-Reduction

A mini-mill like SYSCO only requires a mini-iron plant. There are a variety of direct-reduction processes, either under development or actually operating which are of this scale. In general they give a solid iron product rather than a liquid, so that subsequent steel making processes have to melt as well as refine, and separation of impurities is not as good as in the blast furnace because there is no liquid slag to carry off the impurities.

A successful direct-reduction operation has been the MIDREX process, used by SIDBEC-DOSCO in Quebec. This is a solid-state reduction of pellets by means of reformed natural gas brought in from western Canada by pipeline.

The CO_2 -product gas is used to partially oxidize (reform) the natural gas into CO and H_2 , the heat of the reaction providing the necessary temperature for the reduction of the ore. Two units produce about 1.1 million tonnes per year of 93% iron, the main impurity now being oxygen rather than carbon (the latter 1%) as in blast furnace iron. The attractiveness of the MIDREX process (and others like it) is that the units do not have to be very large to obtain economies of operation, and 0.5 million tonnes per year is a feasible package. Their output compared with capital cost is good; a million-tonne per year plant has a volume productivity of 10.4 tonnes/day/meter³ as compared to only about 1.7 for a comparably sized blast furnace. Of course these units do not make liquid iron so their output has to be melted later. The great thing about a blast furnace is that it is a combination gasifier, reducer, and melter.

When iron is made in the future at Sydney a direct reduction plant of the general MIDREX type would be sensible. However, the steel plant was located where it is largely because of coal, and its long-term viability may remain tied to this fact. Therefore, a direct reduction process which would utilize coal directly, or the reformed gases from the gasification of coal, would seem to be more appropriate. The STELCO-LURGI process is an example of the first.

There are many strategies available, but one that would allow the valuable coking properties of Cape Breton coal to be utilized would be to construct a large merchant coke plant, sell the coke abroad for use only in large efficient blast furnaces, and reform some of the coke-oven gas for local direct-reduction purposes. The developers of both the HyL and MIDREX processes have recently announced an extension of their processes to the reforming of coke-oven gas. The remainder of this strategy would be to pipeline excess coke-oven gas for other industrial or commercial uses, and refine the reduced iron pellets in an electric arc furnace powered by electricity generated by the combustion of lower grade coals.

As might be expected, a great deal of research has been performed on the fundamentals of the kinetics of direct reduction of iron-oxide by reducing gases. It proceeds by a stepwise reduction from Fe_2O_3 to Fe_3O_4 to FeO and finally to Fe. The main kinetic resistance is countercurrent diffusion of gases through the solid layers and is affected by the density of the pellet and impurities.

It should be pointed out that, in general, the efficiency of all these high throughput units depends upon efficiently bringing up the large quantities of raw materials. In this respect we may note that the best reductant is the electron itself, and that it can be moved simply and cheaply along wires. Therefore, there are hypothetical advantages to an electrochemical process for reducing iron oxide to iron. Here we are not suggesting the electroplating of iron from aqueous solution, but from the fused oxide itself. One problem is that these molten oxides exhibit electronic conductivity rather than ionic, and so it comes down to finding some additive which would produce a fused salt from which iron could be plated. This was the kind of technology that allowed the aluminum industry to be successful and might be a worthy subject for research for the iron industry.

Steelmaking

No matter how iron is made from iron oxide, there must be a further refining step to make steel. Liquid iron from the blast furnace contains about 4% carbon, and this must be removed along with the other impurities such as silicon, manganese,

and sulfur. This is accomplished in a variety of batch processes, the chief characteristic being that the oxidation potential of the system is much higher than that in the blast furnace, so that the chemistry of the system is shifted towards much lower carbon contents than the 4% of the liquid iron. For example, 1% carbon steel is a high carbon steel, 0.8% is normal for rail steel, and mild steel around 0.1%. The important requirement for any steelmaking process is a good supply of oxygen. In the discussion to follow it may be noted that technological advances have been made by improving the rate at which oxidant can be supplied to the reaction interface between the oxidizing medium (be it gas or liquid slag) and the liquid iron.

Bessemer Converter vs Open Hearth Furnace

The era of quantity steel, as opposed to cast iron, began in about 1865 when Bessemer patented his process of blowing air through a bath of molten iron. It is fortuitous that iron itself will not oxidize until after carbon and silicon have been removed, and this is what makes the whole thing possible. Bessemer's process was closely followed by the development of the open hearth furnace, and for 50 years the industry saw these 2 processes make essentially all the world's steel. The basic differences in the 2 are worth pointing out as they have relevance today. Figure 3 shows that the metal bath in the open hearth is shallow but large in surface area, and is heated by an overhead flame, while in the Bessemer converter the metal is deep, of small area, and unheated. In the Bessemer process the air bubbled up through the molten iron and, giving a high specific rate of oxidation, resulted in a high production rate (about 100 tonnes steel/h). The capital cost for a given output

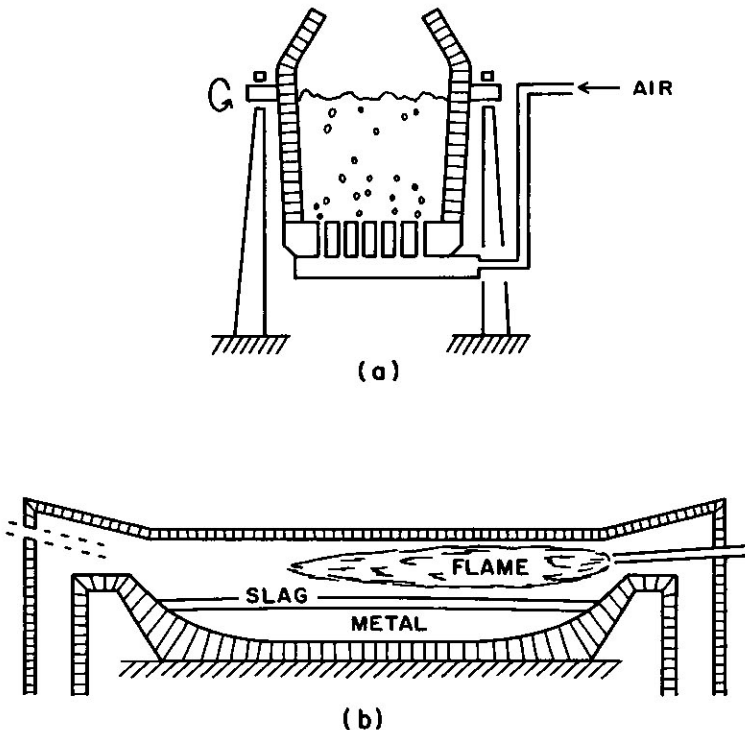


Fig 3 Comparison of configurations of Bessemer converter (a) and open-hearth furnace (b).

was low. However, the converter could not melt scrap, chemistry was not easily controlled, the range of impurities that could be handled was limited, and nitrogen dissolved in the steel. Another problem was the serious attack on the firebrick bottom by iron oxide, although to counter this the converter was made with an easily replaced bottom. The chief virtues of the open hearth furnace were large size, the ability to melt scrap, and controllability. Its disadvantages were that the oxidation rate was limited by the slow diffusion of oxygen (to give a production rate of about 20 tonnes/h), the capital cost was high, and repairs were costly.

The percentage of the world's steel made by the Bessemer process peaked in 1875 at about 80%, and slowly declined thereafter as the open hearth became more popular. The forerunner of the present SYSCO was built in the early 1900's, when the open hearth process was emerging as the dominant technology, and in its day it was a modern integrated facility. By 1950 the conventional OH furnace had reached its peak of use and was making 70% of the world's steel. Furnaces were large (ones of 600 tonnes are still used in USSR) and becoming quite sophisticated.

Electric Arc Furnace

The electric arc furnace began as a means for getting heat into a furnace without using an oxidizing flame; thus scrap could be better melted and as well the temperature and chemistry kept under better control. Vessels tend to be deep and of small surface area, so that oxygen enters the top by diffusion and the specific oxidation rate is low. However the arc furnace is usually used for making specialty steels such as stainless and high-carbon, or for melting pre-reduced pellets, so that there is less requirement for high rates of carbon removal.

Processes Using Gaseous Oxygen

It is interesting to note that the original patent of Bessemer included the possibility of blowing with pure oxygen as well as air. Of course in the late 1800's tonnage quantities of oxygen were not available so this prospect had to wait for a later time.

The war and post-war years saw first Germany, then the United States and USSR, develop tonnage oxygen plants for missile propulsion, and this finally allowed the

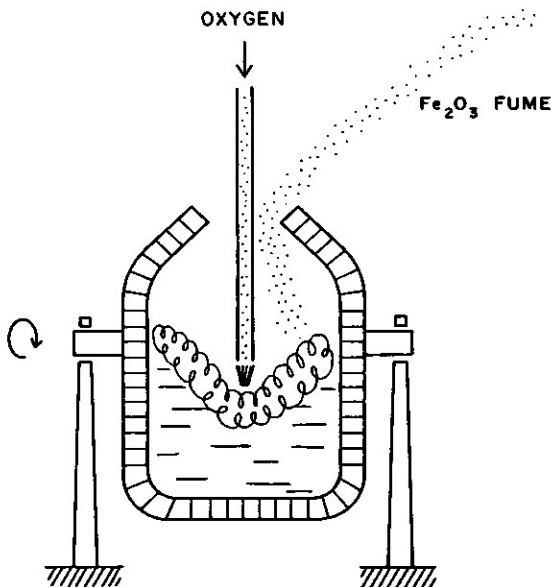


Fig 4 Configuration of basic oxygen process (BOP)

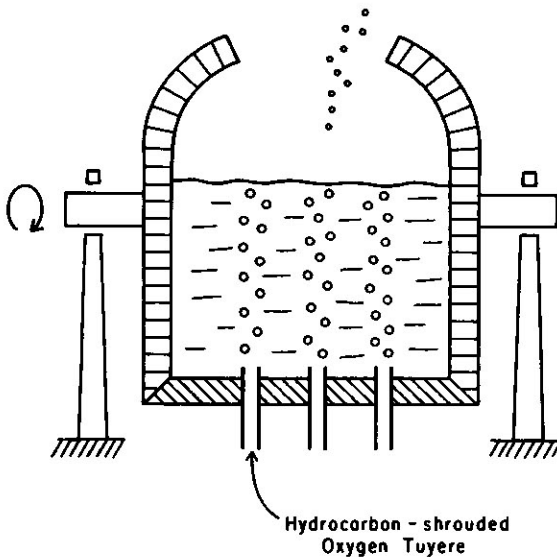


Fig 5 Configuration of Q-BOP

promise inherent in Bessemer's original patent to be at least partly realized. It was in Austria that the LD process was developed and Figure 4 shows the configuration. Oxygen is blown down onto the surface of the metal at such a rate and pressure that a quite violent oxidation occurs, considered to take place mainly at the large reaction interface of an emulsified mixture of metal and slag. This process, which has become called simply the basic oxygen process (BOP) rapidly became popular and after 1970 overtook the OH process in the percentage of steel made. The speed of refining is the important feature. Specific blowing rates of 3m^3 of O_2 /minute/tonne can be achieved for large 200 tonne vessels. This means that 200 tonnes of 4% C. iron, containing 8 tonnes of carbon, can be refined in about 20 minutes. This is a reaction rate of 2.7×10^3 moles/second, and means that only about 100 of these vessels operating continuously could refine the world's steel production. They can melt up to about 25% scrap, and computer control of the blow maintains correct chemistry. A great deal of fine Fe_2O_3 fume is evolved, and of the capital cost of a BOP about 20% has to be expended on controlling atmospheric emissions. It is interesting to note that DOFASCO in Hamilton was the first North American plant to install a BOP.

It was not long before OH furnaces were also equipped with top-blown oxygen lances, and this helped to bring refining times for a 300 tonne furnace down to 5-6 hours. This has prolonged the life of many an OH shop, including SYSCO's. The fume problem is severe because of the large bath area, and in general this configuration is not the ideal one for the top blowing of oxygen.

The most recent development of the BOP is the Q-BOP, where oxygen is injected through bottom tuyeres. This is the logical development of Bessemer's idea, although there is a crucial difference (Fig 5). One of the problems with the original Bessemer converter was the continuous attack of FeO on the bottom refractories and the burning back of the tuyeres. This problem potentially is worse for injection of pure oxygen, and the solution which allows the Q-BOP to function was to shroud

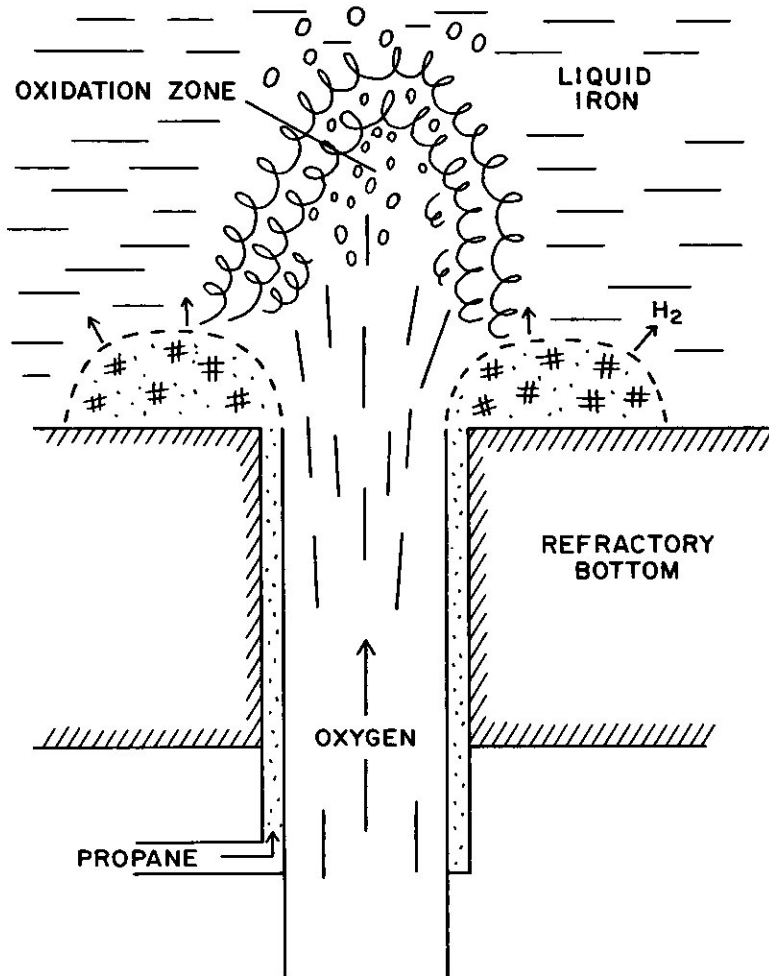


Fig 6 Operation of hydrocarbon-shrouded oxygen tuyere.

the oxygen pipe with an outer annulus through which a hydrocarbon gas (e.g. propane) is passed (Fig 6). The hydrocarbon cracks into hydrogen and carbon as it emerges from the annulus, and as this is an endothermic reaction it cools the end of the tuyere. A porous "mushroom" of iron-carbon is built up at the annulus and protects the pipe and the refractory, although this is still the weak part of the equipment (Parish & Pengelly 1979). One important advantage of Q-BOP over BOP is that there is less fume and less slopping of slag and metal. Blowing rates can be greater, and are beginning to get to the point where reaction rates will be limited by the chemical step at the gas metal interface, rather than by the rate at which oxidant can be brought up to the system. The Q-BOP process has an interesting history and Nova Scotia has a connection with it. Two Montreal engineers working for Canadian Liquid Air, G. Savard and R. Lee, invented the hydrocarbon shrouded tuyere in the 1950's, and some of their first, small-scale trials were carried out in the steel plant in Sydney. After some years the rights to this invention were sold to a German firm which developed it into a workable steelmaking process. U.S. Steel now has the North American rights, and it was they who called it Q-BOP, Q for "quiet, quick and quality".

It was mentioned that OH furnaces became equipped with top blown oxygen lances to speed up steelmaking, and in like fashion when the hydrocarbon-shrouded tuyere became available this also was adapted to the OH. SYSCO tried this several years ago in a process known as SIP, for Submerged Injection Process. Details of the process were not made public, but apparently there were several tuyeres per furnace, and the productivity was high. However, the experiment was discontinued, probably because of severe refractory wear and general unreliability. It should be noted that the bottom of a Q-BOP vessel is relatively small, has 10 or so tuyeres, and when too many tuyeres burn back or plug up, the entire bottom can be replaced in a reasonably short time. The OH furnace has a relatively large bottom which cannot be replaced easily, and presumably fewer tuyeres are used. The depth of metal in an OH is not great, and it is depth of metal that makes bottom injection so efficient.

Bottom injection of oxygen seems to be the technology that will become dominant, as discussed in a recent paper by Parish and Pengelly (1979). The SIP process shares some of the advantages of this technology, and it may make sense to convert existing OH furnaces to this process. However, it should be considered only as an interim solution, the final one being a properly configured Q-BOP installation.

Summary of Steelmaking Processes

It should be pointed out that oxygen processes require that a large quantity of carbon be oxidized. The exothermic heat of that reaction allows some scrap to be melted, and allows the melt to attain the high temperatures required for subsequent operations such as vacuum degassing and continuous casting. The Q-BOP or BOP are ideally suited for refining the huge output of modern blast furnaces. However, iron from a direct reduction plant such as a MIDREX plant contains much less carbon, and a different refining process would be used. At SIDBEC-DOSCO the refining step is carried out in a large electric arc furnace. This might have to be the solution for SYSCO for the long run, with low grade coal used to generate electrical power.

Figure 7 is a comparison of steelmaking methods from Bessemer's time, showing how processes have taken over from one another. It is apparent that the BOP process is destined to predominate, in either the top or bottom blown version. At the same time the electric arc process will continue to grow, and perhaps what we will see in the future is a hybrid process combining both bottom blowing of oxygen with assistance from electric arc or electric plasma. The advantage would be in the proportion of scrap that could be utilized; this is now down at about 20% for a Q-BOP.

However, it has been remarked (Callenfels 1979) that steelmaking, and indeed a whole range of capital intensive industries, is changing over from a period of

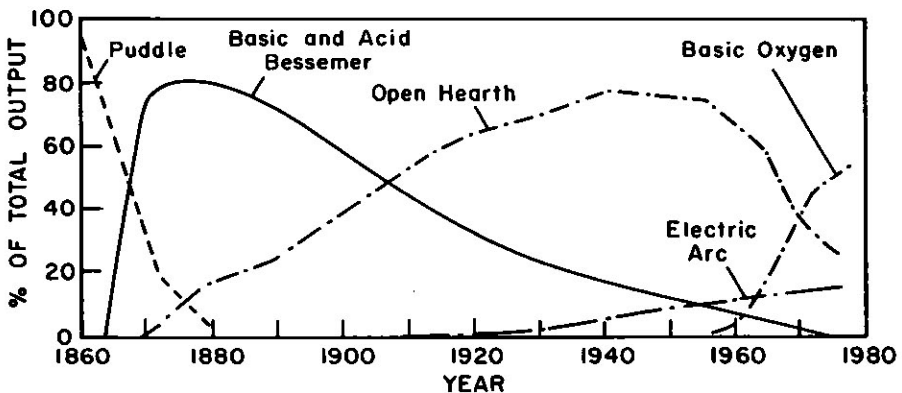


Fig 7 Development of some processes in the steel industry.

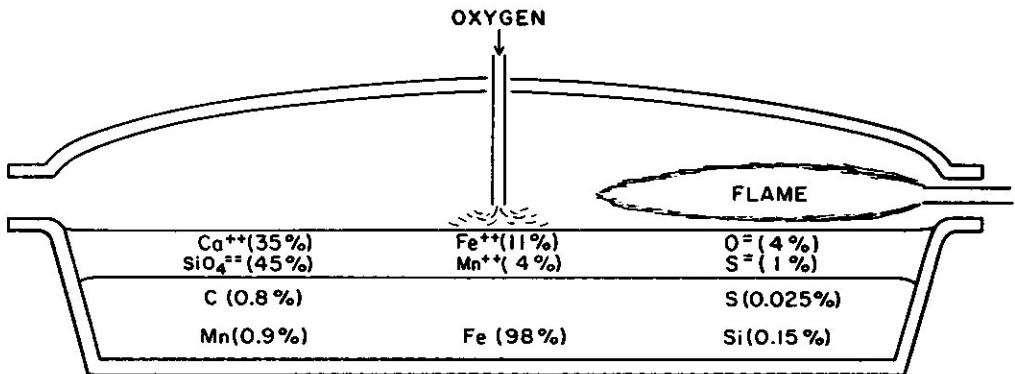
"technology push" to "market pull". In the past nearly every option that technology had to offer could be absorbed easily by a rapidly expanding market. Now we have the stagnation that is inherent in a mature economy, and it will be society as a whole that will determine the "market pull" and thus set the pattern and rate for technological innovation.

To finish this discussion of steelmaking it would be appropriate to illustrate its chemistry. Figure 8 gives some representative concentrations (in weight %) for an open hearth operation; other steelmaking processes would not be very much different. The important difference between blast furnace slag (Fig 2) and OH slag is that the latter contains free O^{2-} ions, indicative of the high oxygen potential of the system, and that for the same reason the slag contains iron ions. This represents a potential loss of iron, so that when possible the OH slag is recycled back into the blast furnace. Slag chemistry is an important topic for research and will be mentioned later.

Some Research Problems In Nova Scotia

Industrial Research

We shall consider briefly two industrial-scale research programs. The first one was a cooperative program on the problem of sulfur in steel, financed by an NRCC grant to SYSCO under the Industrial Research Assistance Program scheme, and carried out by some members of AGRIM. The physical-metallurgical reasons why sulfur is deleterious in steel is a subject too large to pursue here, but it may be pointed out that sulfur rarely can be tolerated in concentrations over 0.05%, and for some sensitive grades of steel the maximum sulfur may be limited to 0.005%. Figure 9 shows MnS inclusions in a piece of reinforcing rod which had failed in a bend test. Figure 10 shows a scanning electron microscope image of particles of FeS_2 in coal; as mentioned previously the coal which is used to make coke is the source of the sulfur-in-steel problem. Figure 11 is an indication of how the sulfur partitions among the various phases of the overall steelmaking process; the numbers given are representative only, and will vary widely from steelplant to steelplant. Members of AGRIM investigated, among other things, methods of removing sulfur from coal, although that is not part of this discussion. SYSCO worked on means of removing sulfur from the liquid iron as it is in transit between the blast furnace and the open hearth. This was not really research or innovation, but was an effort to acquire the state of the



THESE FURNACES HOLD SEVERAL HUNDRED TONS OF LIQUID STEEL

Fig 8 Chemistry of the open-hearth furnace. Steel shown is typical of rail steel.

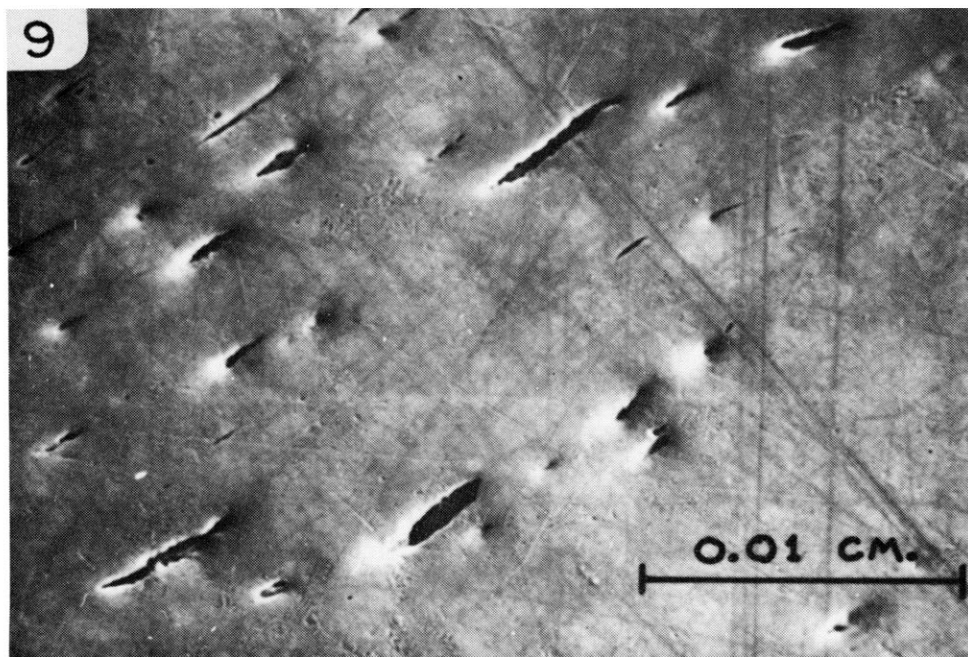


Fig 9 Manganese sulfide inclusions in steel.

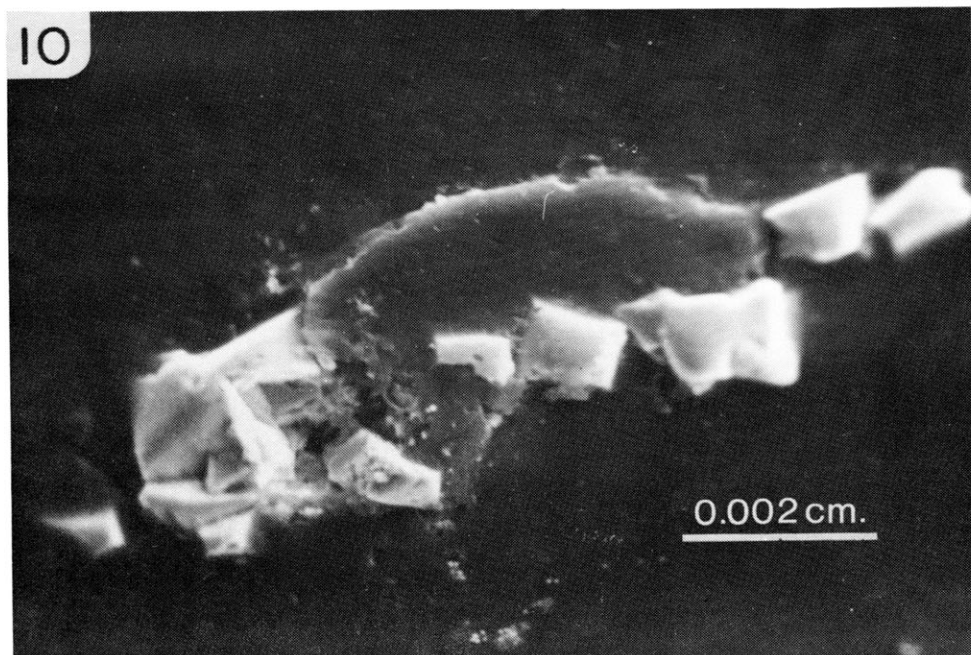


Fig 10 Iron sulfide (FeS_2) particles in coal from the Prince Mine, Cape Breton.

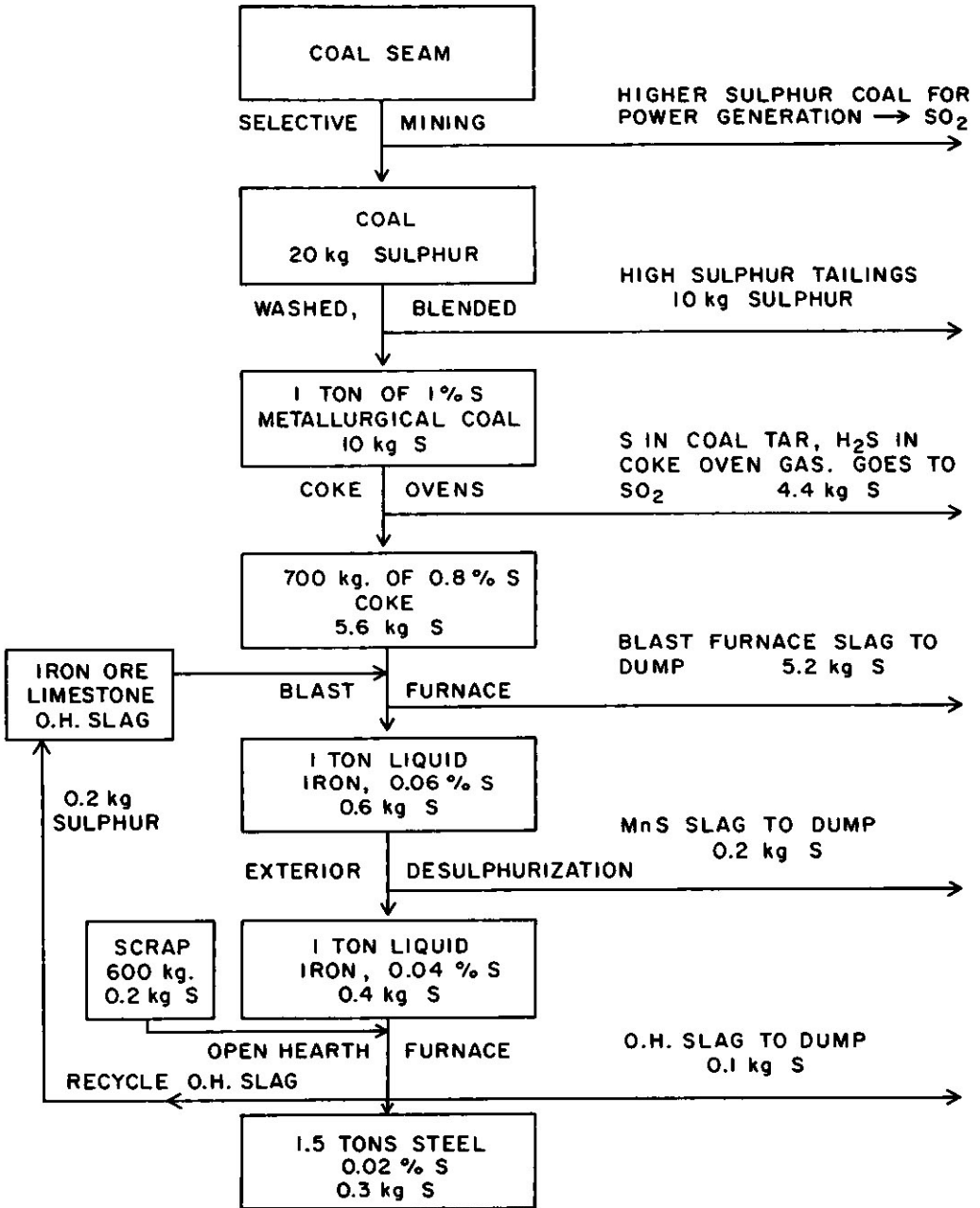


Fig 11 Sulfur pathways in steelmaking (ton = tonne).

art. In this case the final decision was to use "Magcoke", porous coke impregnated with magnesium metal. When a container of it is plunged beneath the surface of the liquid iron it causes a reaction between sulfur and vaporizing magnesium to give an MgS slag which can then be skimmed off the surface. Another part of the project was adding rare earth metals (such as lanthanum) to the steel as it is tapped; instead of long stringy inclusions of MnS (Fig 9), globular inclusions of mixed oxysulfides are obtained, and these are not so deleterious. This last work was a joint project of SYSCO and the Technical University of Nova Scotia.

A second piece of industrial research is on the problem of hydrogen in steel, the subject of a contract between the Atlantic Research Laboratory (NRCC) and SYSCO. Hydrogen dissolves in liquid steel as the atom (largely derived from the dissociation of water vapor) to a maximum of about 20 ppm. Its solubility decreases as the steel is cooled, particularly after the gamma to alpha transition. Hydrogen diffuses to grain boundaries, inclusions, and other nucleating centers, comes out of solution, and reforms to yield molecular H_2 . The pressure of hydrogen that may be generated in such microvoids can become very large, hundreds of atmospheres. In some cases the strength of the steel is exceeded, and shattercracks are formed. These can be serious if not detected in the finished products, such as the rails which are SYSCO's main products. The present method of avoiding shattercracks is to take the hot rails as they are rolled and put them into insulated tanks, giving them the proper combination of time and temperature to allow atomic hydrogen to diffuse out to a safe 3 ppm. Hydrogen, being small, diffuses readily.

The present contract is on various aspects of the possibility of allowing unfinished steel, at the bloom size of 10" x 16", to soak in tanks. Experiments include work on the effusion of H_2 from cooling rails and blooms, such as the actual detection of hydrogen by gas chromatography, and computer simulations on the buildup of molecular hydrogen within steel sections of various sizes. One interesting series of experiments being done by R. Hay of Ecole Polytechnique employes "acoustic emission". The technique is a means of monitoring the formation of shattercracks by "listening" for them with acoustic transducers. Sound signals registered because of energy release upon formation of cracks within the bloom are fed to a microprocessor where they are analyzed for energy levels and position of origin within the bloom. Preliminary results indicated that high energy acoustic events correlate well with the formation of shattercracks. Acoustic emission may be a useful tool for determining in a non-destructive manner whether a particular bloom-cooling technique reduces the shattercracking phenomenon.

Fundamental Research

On a more fundamental laboratory level, it may be noted that steelmaking involves two quite different types of chemical solution: (1) a metallic solution with liquid iron as the solvent and containing solutes such as C, O, H, Si, Mn; (2) ionic slags containing cations such as Ca^{+2} , Mg^{+2} , Fe^{+2} and anions such as O^{-2} , SiO_4^{-4} , S^{-2} . These solutions are immiscible and the equilibrium between them, and the kinetics of exchange between them and the gas phase, are fruitful subjects for research.

The basic chemistry of the oxidation of solutes from liquid iron, especially carbon, is the essence of steelmaking. Figure 12 is a representation of the likely steps in the gaseous oxidation of carbon from iron (Hayer & Whiteway 1973). (A somewhat similar scheme, but one which includes charge transfer steps, may be envisaged when the oxidant is the O^{-2} , Fe^{+3} of a slag.) We begin with oxygen in the bulk of the gas phase, and carbon in the liquid. Oxygen begins to flow to the metal surface but has to diffuse through an inevitable stagnant gas layer next to the metal. This

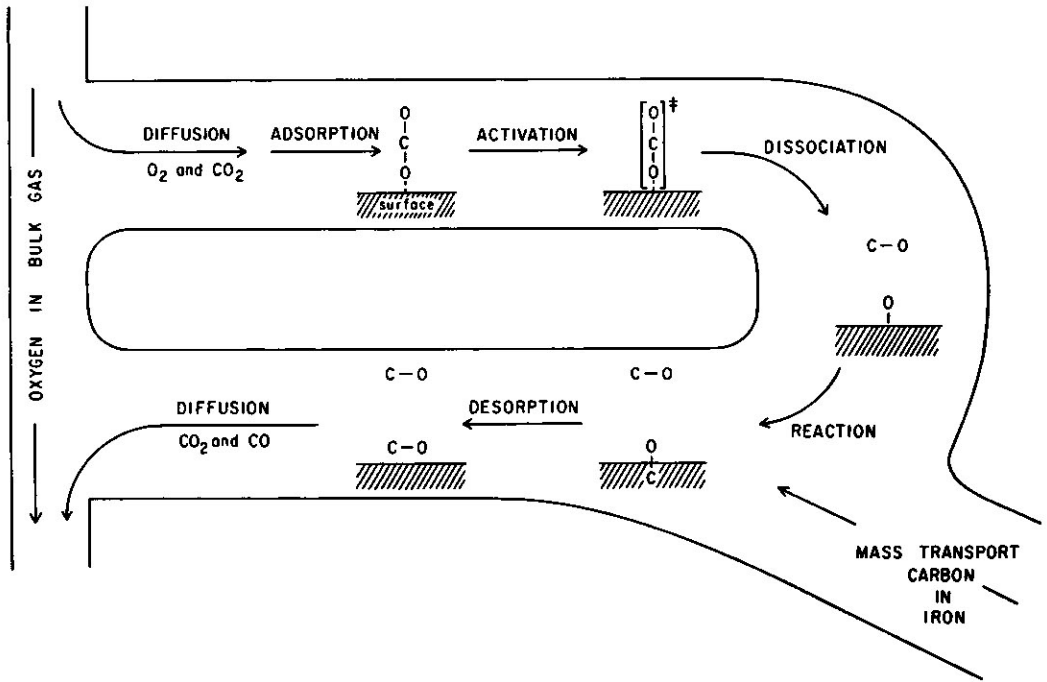


Fig 12 Steps in the oxidation of carbon from iron, using gaseous oxygen.

layer may be thick or thin, depending upon gas-flow factors such as turbulence. In the diffusion layer the oxygen reacts with the product of oxidation, CO, which is diffusing out in a countercurrent fashion. The oxidant now is CO_2 , which continues to diffuse to the metal. This oxidant is adsorbed on a free surface site on the liquid iron, activated, and dissociated into a CO portion which desorbs, and an O portion which remains. This O reacts with a carbon atom diffusing up from the bulk of the molten iron to form adsorbed CO which finally desorbs and is carried out of the system. As the CO diffuses in the stagnant gas layer, it reacts with incoming oxygen as mentioned, and continues diffusing out as CO_2 . Thus CO_2 is both the product and the reactant.

Each of the above steps contributes some kinetic resistance to the overall rate. However, at steelmaking temperatures of around 1600° , the intrinsic rate of reaction between adsorbed oxygen and carbon is very high, and seldom is rate determining. Figure 13 shows some data for the intrinsic rate, as well as an example of a typical laboratory experiment in which the actual rate fell well below this (Hayer & Whiteway 1973). Thus it is commonplace to find that it is the rate at which the oxidant can be delivered, through the stagnant gas layer next to the metal, that is rate determining. That is why the evolution of steel-making processes has been in the direction of maximizing the flow of oxygen to the metal.

Figure 14 is our concept (Whiteway et al. 1975) of the relationship among CO_2 , CO and O_2 in the stagnant gas layer, assuming thermodynamic equilibrium. We have used a stabilized-zirconia EMF cell to probe down into the gas phase over oxidizing carbon, and have shown that this picture is largely correct. However, very near the

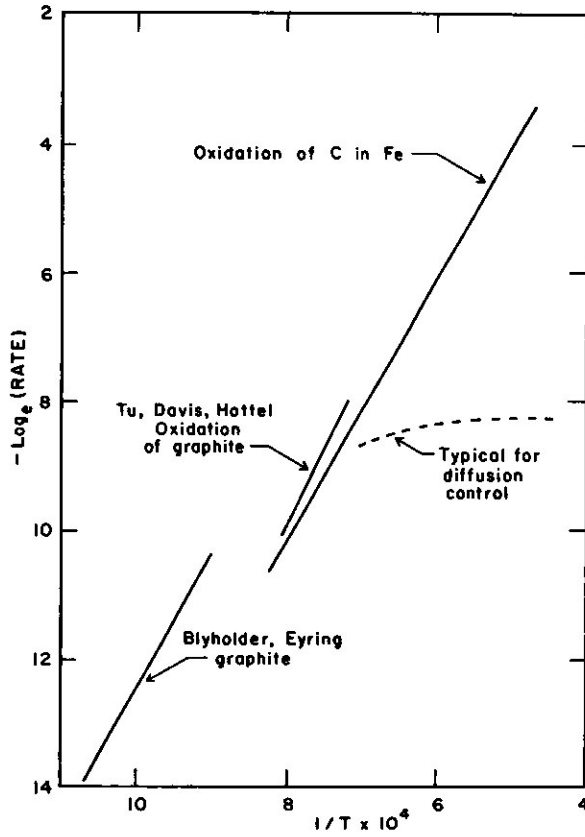


Fig 13 Intrinsic rate for oxidation of carbon by gaseous oxygen, including pure graphite and carbon dissolved in liquid iron.

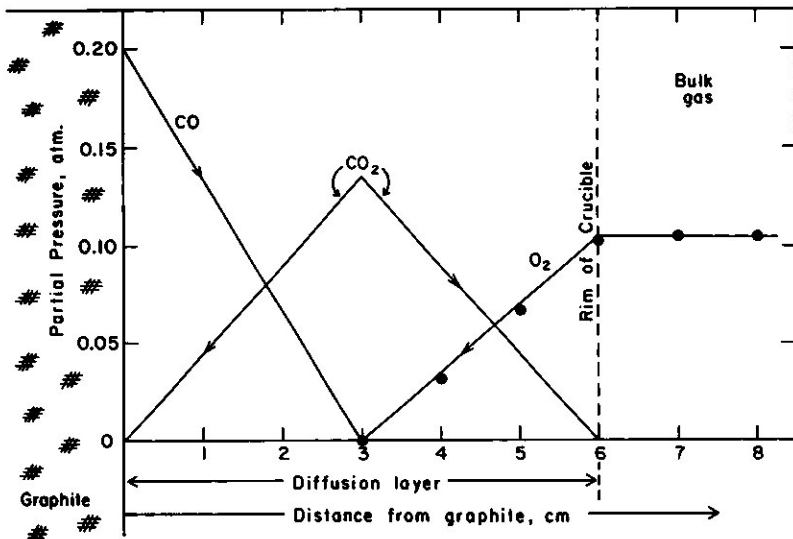


Fig 14 Relation of the species in the gas phase over oxidizing graphite.

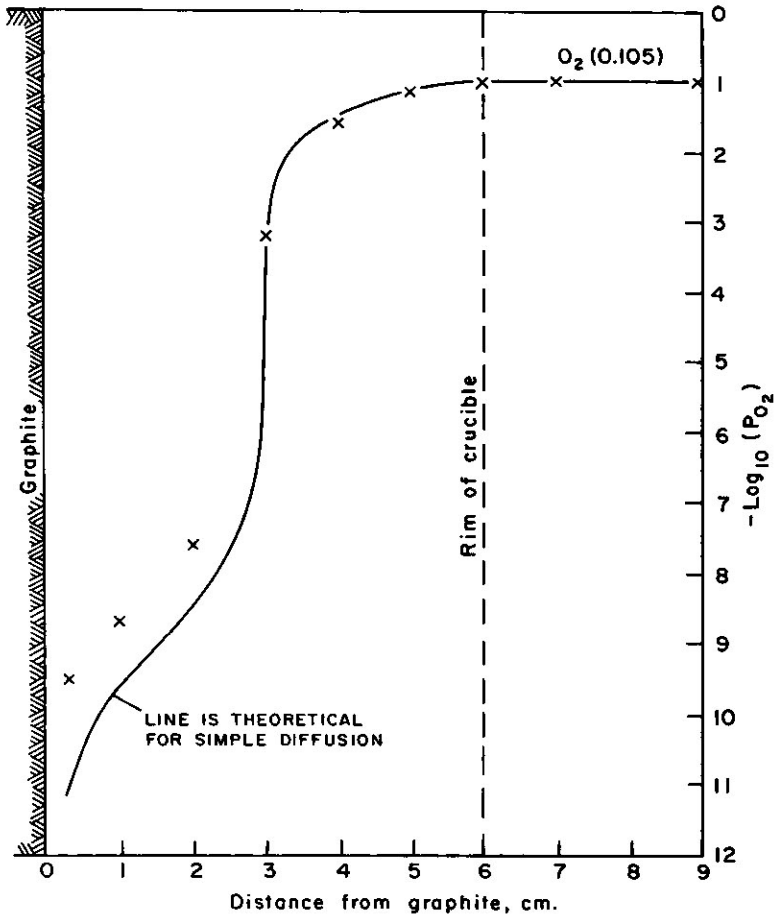


Fig 15 Experimental oxygen potential in the gas phase over oxidizing graphite.

graphite (Fig 15) the observed partial pressures of O_2 (of the order of 10^{-9} atmos.) are higher than that calculated from equilibrium conditions, indicating that some O_2 is escaping reaction with CO , and presumably this oxygen can react directly with the surface. If this is true under mild laboratory conditions it must be even more true when pure O_2 is lanced down onto a liquid iron surface.

Sulfur, when dissolved in liquid iron, is surface active. Therefore, there is some reason to expect that it could occupy surface sites and so render them unavailable for other reacting species such as CO_2 . This was our (Hayer & Whiteway 1973) explanation for the experimental finding that while sulfur itself was not oxidized it slowed down the rate of oxidation of carbon (Fig 16). The behavior could be modelled by a scheme which took into account the competition for sites between CO_2 and S. These experiments are typical of many we have done on the kinetics of reaction of gases with solutes dissolved in liquid iron.

Turning to the investigation of the chemical nature of slags, I point out the great amount of work carried out at ARL by C.R. Masson and associates. Realizing the importance of the concept that slags are ionic, and that the silicate monomer SiO_4^{-4} tends to polymerize, Masson (1973) went on to develop models for the constitution of basic slags. The industrial importance of the concept of polymerization

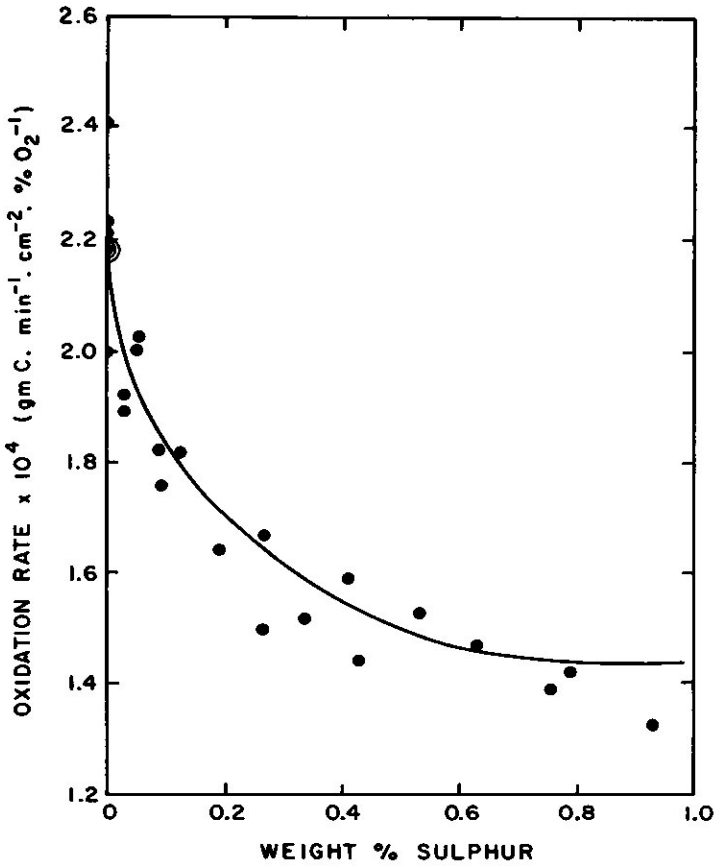


Fig 16 Effect of sulfur on the oxidation rate of carbon from liquid iron.

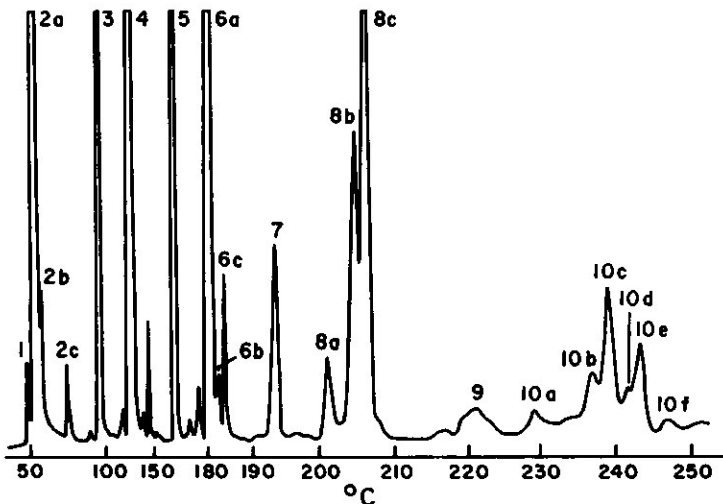


Fig 17 Typical chromatogram for open-hearth slag. The parent ions corresponding to some of the peaks are: 2a = O⁻²; 4 = SiO₄⁻⁴; 6a = Si₂O₇⁻⁶; 8c = Si₃O₁₀⁻⁸.

lies in its connection with the concentration of free O^{2-} , which is a measure of the oxidation potential of a slag, and its connection with the viscosity of slags. Masson and his co-workers (Masson et al. 1974; Calhoun & Masson, 1980) have also worked on the problem of detecting experimentally these ionic polymers, using a combination of gas chromatography and high-resolution mass spectrometry. Figure 17 shows species that occur in OH slags; these are gas chromatographic peaks, and include such identified species as $Si_2O_6F(5-)$, $Si_4O_{12}(8-)$, $Si_4O_{12}(9-)$.

The viscosity of slags is an important industrial parameter, as a very viscous slag can increase refining times. We have developed (Caley et al. 1977) a rotating spindle viscometer which determines viscosity by measuring the torque on a rotated ceramic spindle. One application was to examine the relative fluxing powers of fluorspar (the usual flux added to reduce the viscosity of OH slags), ilmenite (a titanium ore), and strontium oxide. Figure 18 shows that SrO is a relatively poor flux.

Conclusion

I have attempted to give a picture of the present state of the art in steelmaking, the directions it may take, where Nova Scotia is now, and how Nova Scotia might move. It has to be admitted that the directions available to Nova Scotia are dictated by political, rather than technological, considerations. In addition I have given a few examples of industrial scale research and development being conducted in Nova Scotia, as well as some relevant laboratory-scale experiments. Many people have been involved in the research work quoted, and although not cited specifically, their contribution must be acknowledged. My exposure to the steel industry has been made possible by many friends at SYSCO, to whom I owe thanks; they labor at their craft in arduous circumstances.

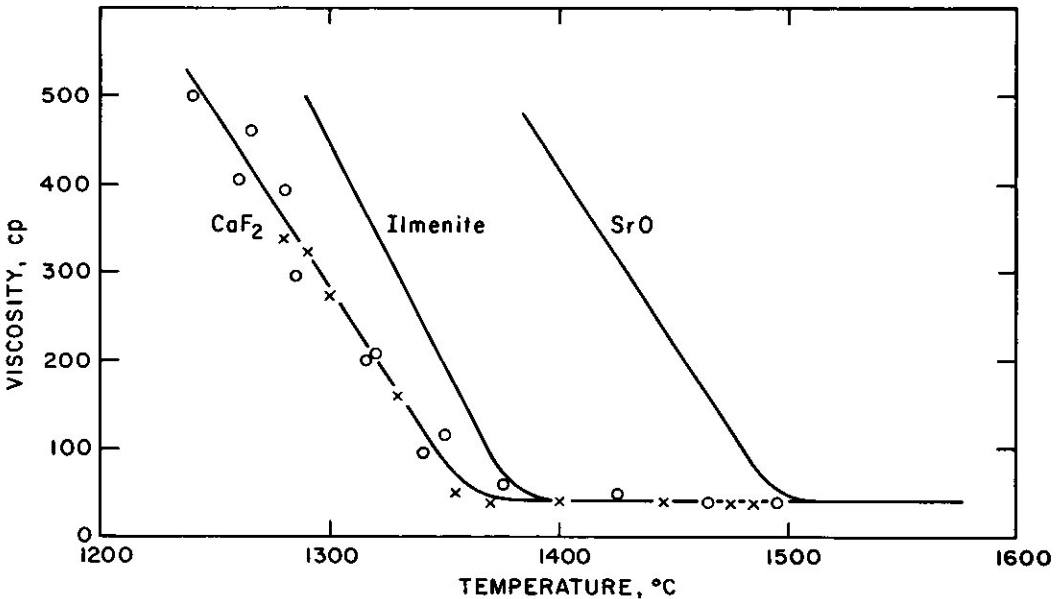


Fig 18 Viscosities of open-hearth type slags with various additives.

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