GRAPHITE ELECTRODE AND NEEDLE COKE DEVELOPMENT

Rick Adams, ConocoPhillips Company, 600 North Dairy Ashford, Houston TX 77079, USA
Wilhelm Frohs, SGL Group – The Carbon Company, Werner-von-Siemens-Str. 18, 86405 Meitingen, Germany
Hubert, Jäger, SGL Group – The Carbon Company, Werner-von-Siemens-Str. 18, 86405 Meitingen, Germany
Keith Roussel, ConocoPhillips Company, 1000 South Pine, Ponca City, OK 74602-1267, USA

Summary

The booming Asian economies are driving the recent increase in steel production. Although BOF steel production growth is much stronger than EAF, the outlook for EAF is promising due to increasing substitution of steel scrap by DRI and pig iron, as well as an increase in electrical energy supply in China. The favorable operational reliability of AC-furnaces is the reason that most new furnace projects will use AC technology, with preferential 600 mm (24") diameter graphite electrodes. The need to further increase the efficiency in EAF steel melting will drive greater usage of combustion energy and more gas tight furnace design in order to reduce energy losses. This will increase oxidation and the thermal stress requirements for graphite electrodes. The quality of the key raw material, needle coke, must be improved to deal with these higher thermal stress loads. Efforts to improve graphite electrode production technology will also support this goal. Legislation and taxation on CO_2 release may place additional constraints on the intensive use of combustion energy in EAF's, particularly at the local level. However, there is no competitive alternative technology for EAF's anticipated for the near-term.

Steel Market

The production of steel strongly increased in the beginning of the 21st century with the rapid growth of the Asian economies. Total production of steel exceeded 1.1 billion tons in the year 2004 and is expected to further grow to above 1.2 billion tons in 2011 (fig. 1). About 66 % of the world's steel is produced in integrated steel works in basic oxygen blast furnaces (BOF). The remaining 34 % is produced in electric arc furnaces (EAF) from steel scrap. The projected annual increase in EAF steel production of about 3 % will be provided by China and other Asian economies including India (fig. 2). Steel production in the Americas and Europe will remain stable or slightly decline. Although BOF steel production growth is currently much stronger in China than EAF, 50 % of the total world's growth in EAF is contributed by China. This country will provide substantial long term potential in EAF capacity increase as electrical energy supply improves and more scrap is available.

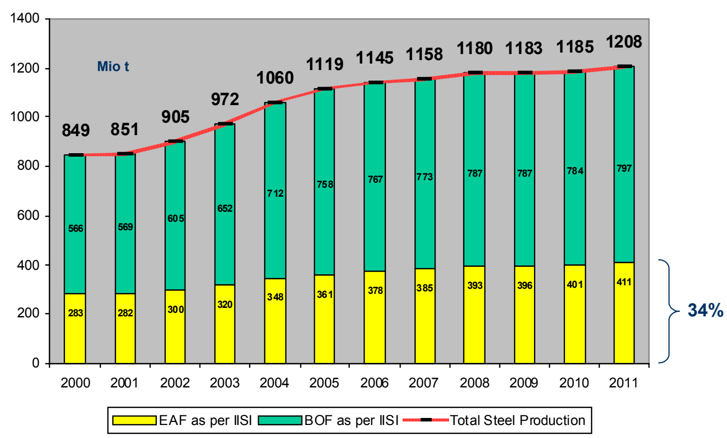


Fig 1. Global Steel

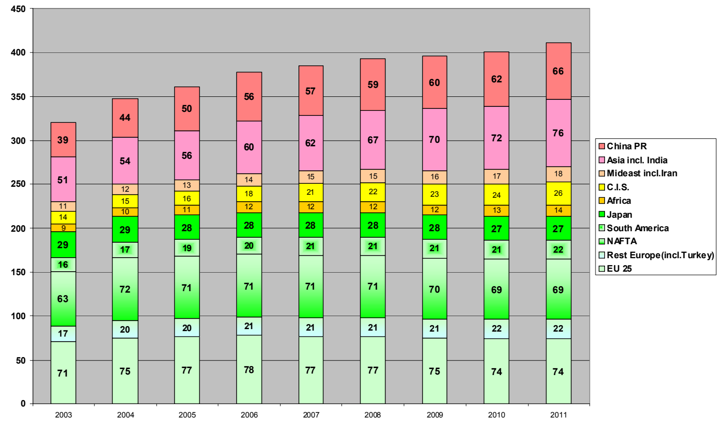


Fig 2. EAF steel production by region (source: IISI and SGL Group internal figures)

The current share of EAF steel and the forecasted growth in EAF steel production would not be possible with the use of steel scrap only. The addition of pig iron and directly reduced iron to the EAF process is required and will provide the necessary raw material sources for the predicted EAF capacity growth scenario (fig. 3).

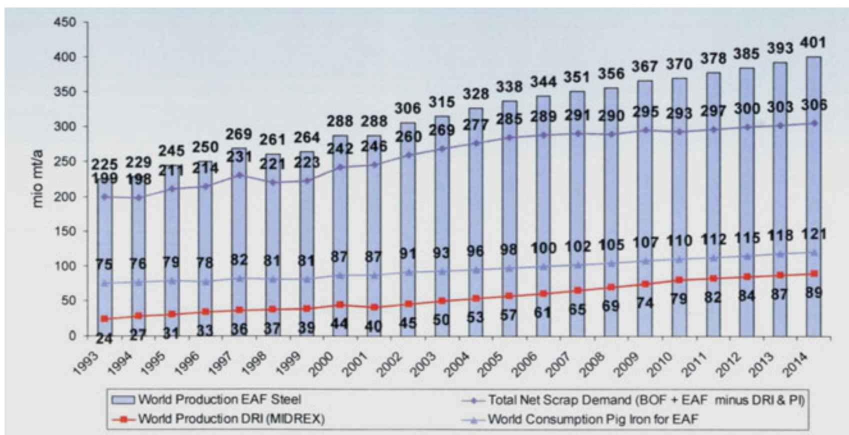
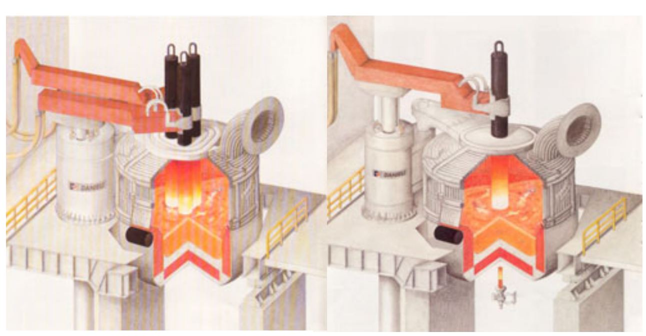


Fig. 3 Pig iron and DRI for EAF steel production (source: IISI and SGL Group internal figures)

Electric Arc Furnace

Significant growth in EAF capacity for steel scrap melting took place after World War II with the availability of steel scrap and favorable low capital cost -five times less- of these so called mini mills compared to BOFs. The main EAF components are the furnace vessel, the roof to cover the vessel during operation and graphite electrodes (GE) for the electric current. Fuel burners and gas lances support a rapid scrap melting.
Two EAF systems are prominent, the traditional AC (alternating current) and the DC (direct current) furnace (fig. 4). The AC furnaces use three graphite electrodes (GE) while the DC technology uses one GE which uses the bottom of the furnace as the anode for current conduction. The most typical GE diameter is 600 mm (24”) in case of the AC furnace. DC furnaces operate with GE in the diameter range of 700 mm (28”) to 800 mm (32”). These big diameter electrodes became necessary to carry the high currents which can reach up to 180 kA. (fig. 5). Typical AC furnace parameters (600 mm diameter) are 50 –70 kA current, 600 – 900 V voltage, tapping weights 80 to 130 mt. steel, and tap to tap times of about 60 – 90 minutes.



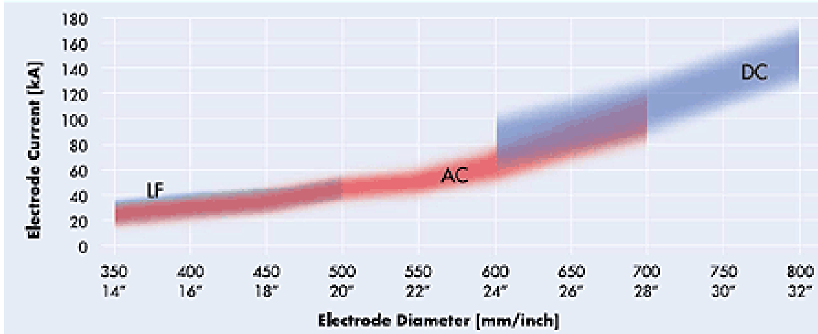
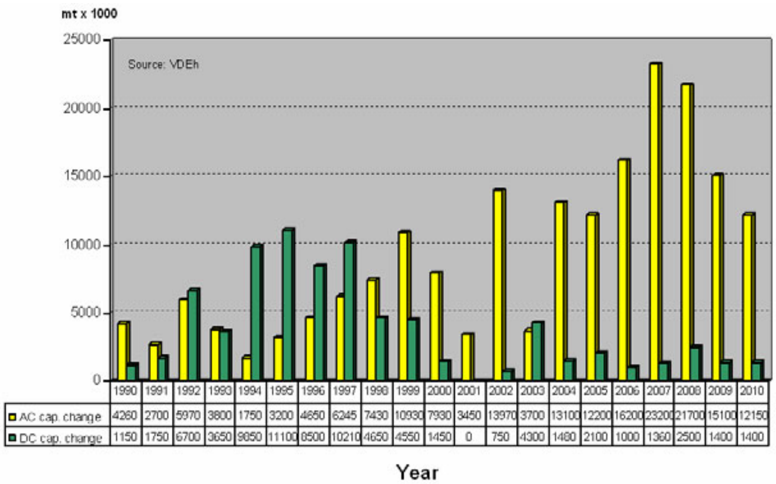


Fig. 5 Electrode current and required electrode diameter

Both furnace types have advantages and disadvantages. The DC technology has for example lower impact on the electrical grid (power fluctuations, e.g. flicker) compared to AC furnaces. On the other hand, the reliability of the bottom anode has never been completely solved. The DC technology boomed in the 1990s, but most new furnace projects today are again AC-type furnaces with GE in 600 mm (24") diameter (fig. 6). Reason for this recent trend is the better operational reliability and thus better economics of AC-furnaces compared to DC-furnaces.



	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010
AC cap. change	4260	2700	5970	3800	1750	3200	4650	6245	7430	10930	7930	3450	13970	3700	13100	12200	16200	23200	21700	15100	12150
DC cap. change	1150	1750	6700	3650	9850	11100	8500	10210	4650	4550	1450	0	750	4300	1480	2100	1000	1360	2500	1400	1400

Fig. 6 AC / DC nominal capacity change

Graphite Electrode Consumption

The consumption of GE can be separated in continuous and discontinuous modes (fig. 7). The continuous consumption is oxidation on the surface of the GE and sublimation at the tip where the temperatures are far above 3000°C. Under normal operation conditions today the continuous consumption accounts to about 80 to 85 % of the total consumption. About 20 % of the consumption is discontinuous, so called stub-end losses and spalling at the tip of the electrode. A nightmare for steel melters are breakages in the electrode and in the area connecting electrode sections (usually with a separate graphite pin).

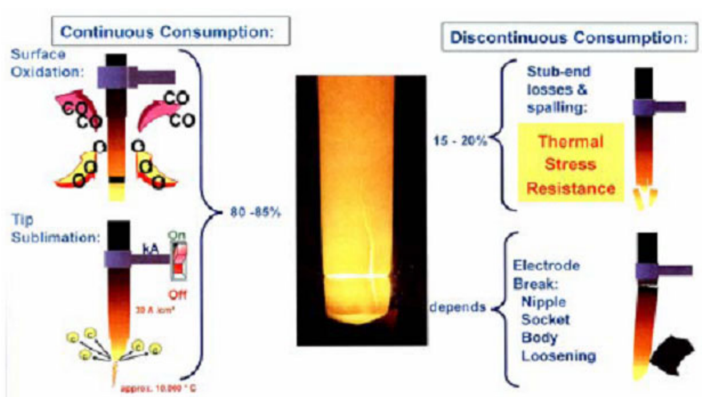


Fig. 7 Consumption modes of graphite electrodes

SGL Group has developed a computerized furnace model that is able to predict the graphite GE consumption for different EAF operational parameters as well as for different GE diameters and physical properties (1). Thus this model is frequently used to advise our customers in their process optimization.

The joint area is a critical area because there is a discontinuity in the material. Before the 1970s it was common to use a male / female connection where the socket and the screwed area were machined from the electrode material. But soon it became obvious that this type of connection was not sufficiently robust at that time to withstand the increasing power and mechanical demand in EAF furnaces. Also the tremendous material losses during machining of the male / female joints and the remaining resultant short electrodes led to the introduction of specially designed connecting pins. With these high strength graphite pins the mechanical robustness was improved. The tailoring of physical properties -i.e. of the compatibility of GE and pin CTEs- contributed to maintaining a closed joint connection during operation. Progress in modern Finite Element Modeling has allowed the geometric optimization of joint details (2, 3). Low CTE needle coke grades has enabled the production of pins with in-axis CTEs being close to zero, which helps to maintain the preset tension between the socket areas of a hot joint after the joining operation.

The consumption of GE is counted in kg/t of steel produced. Whereas the GE consumption had been around 7 kg/t in the 1960, it has been reduced on average below 2 kg/t these days (fig. 8). At specific operational conditions consumption figures of below 1 kg/t have been achieved.

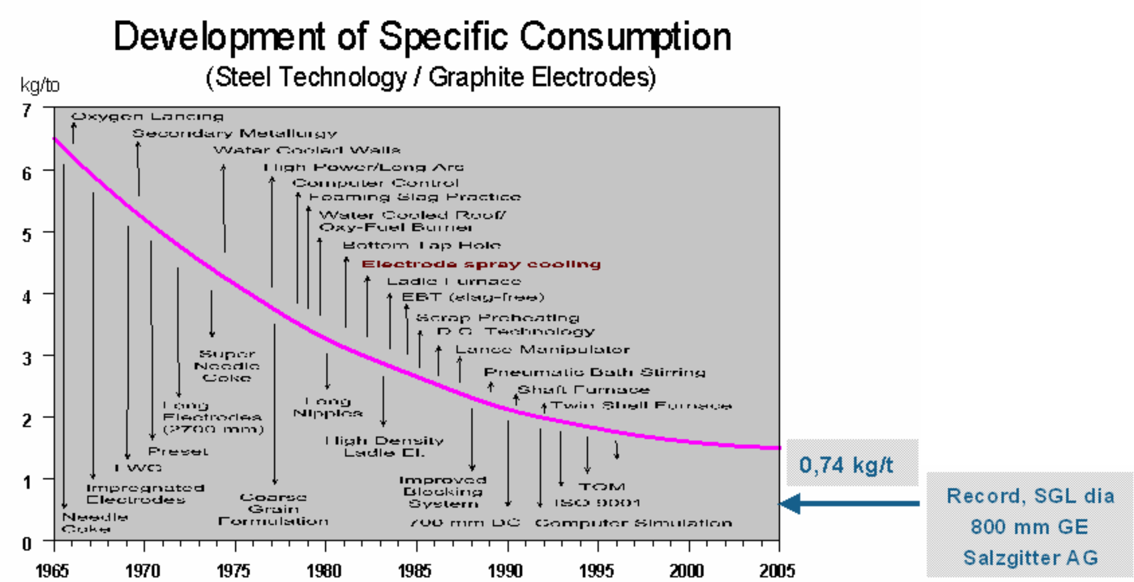


Fig. 8 Reduction in graphite electrode consumption

One of the most efficient improvements in furnace operation was the spray cooling of GE with water. This spray cooling keeps the electrode surface temperature below 500°C and thus stops the oxidation of the GE above the roof. Most important for the improvement of GE was the development of needle coke starting in 1960 with extensive use in the graphite electrode market during the 1970s.

That GE do even survive hours of operation at these extreme thermal conditions without immediate disintegration is due to the unique properties of graphite. Graphite is a good conductor of electricity and heat. It does not melt under these high temperatures and its mechanical properties even improves up to about 2200°C. The coefficient of thermal expansion (CTE) is even negative in the graphite layer direction (4.).

The translation of these fundamental properties in their optimal arrangement into GE determines the electrode quality. One key parameter for GE is the thermal stress resistance (TSR) factor which is highly determined by the raw material used (fig. 9).

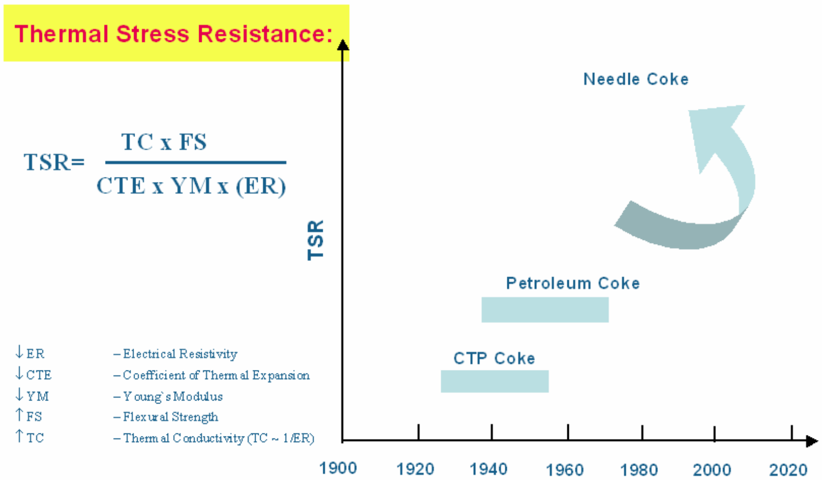


Fig. 9 Steps in raw material based graphite electrode quality expressed by thermal stress resistance

Early GE production started with coke made from coal tar pitch. The availability of petroleum coke from crude oil conversion in special delayed coker units –first delayed coke 1935- replaced coal tar pitch coke over the years. By the 1970s needle coke had replaced nearly all other raw materials in the production of high quality GE. The low CTE and the excellent graphitizibility of this needle coke was a breakthrough in the quality of GE and stimulated the increase in EAF power input.

The production of modern needle cokes requires the separation of the heaviest fraction of an aromatic feedstock in a fractionation unit. This heavy fraction is then fed into a coker furnace to heat it up to coking temperatures. This furnace's operation is critical in a delayed coking process to ensure that the coking of the feed is "delayed" until it reaches the coke drums and coke formation in the furnace is minimized. The coke is formed in one of two coke drums in a semibatch operation. While coke is formed in one drum, it is removed from the other drum (fig. 10).

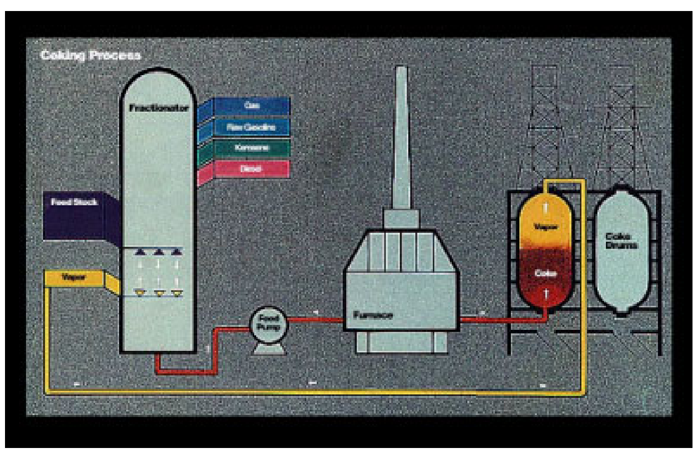


Fig. 10 Delayed coking process

Once the "green" coke is produced in the coke drum and removed, it is then sent to a calciner where it is heated to around 1400 °C to remove the volatile material remaining from the coking process and start the crystal growth process.

Contrary to the progress in coke over the years, technical progress on the binder pitch raw material was much lower. Although there has been some changes, in particular a reduction in Quinoline Insoluble content (QI) in Europe - which did support lower electrical resistivities - most changes did not happen on purpose but were due to changes in the coke oven process. Today in the framework of the European Chemical Legislation

(REACH) we have to expect more limitations in coal tar pitch production, handling, and manufacturing therewith due to its polyaromatic hydrocarbon (PAH) content.

Electrode Manufacturing

The invention of needle coke had also influenced the manufacturing of GE (fig. 10). The most popular forming process for GE is the extrusion through a cylindrical die. The needle-like morphology allows the production of highly anisotropic GE having with grain physical properties as desired, i.e. low in-axis CTE and high in-axis electrical conductivity.

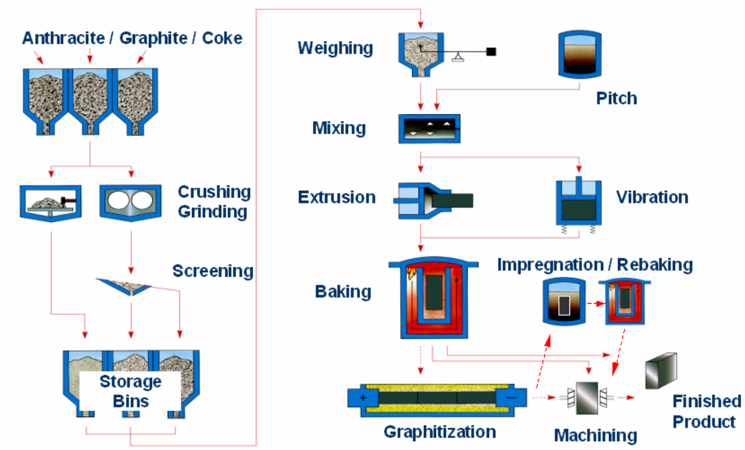


Fig. 10 Manufacturing of graphite electrodes

With higher electrical power input in EAFs, larger diameter electrodes were requested. As a result, higher thermal stress in the GE was the consequence. The ceramic toughening principle to hinder crack propagation on bigger particles led to the introduction of coarse grain formulations of the coke used in the GE manufacturing. With the diameter extension to ultra large diameter GE (700 mm – 800 mm) – SGL was the first to produce 800 mm diameter GE - the maximum grain size now exceeds 20 mm (fig. 12). (5). This change in formulation was a challenge for the refineries in coke cutting, crushing, calcining , handling and transportation. A further increase in GE diameter in DC application seems unlikely these days. A trend to moderate diameter increase (650mm, 700mm) might even happen on new AC-furnaces with large tapping weights up to 250 t.

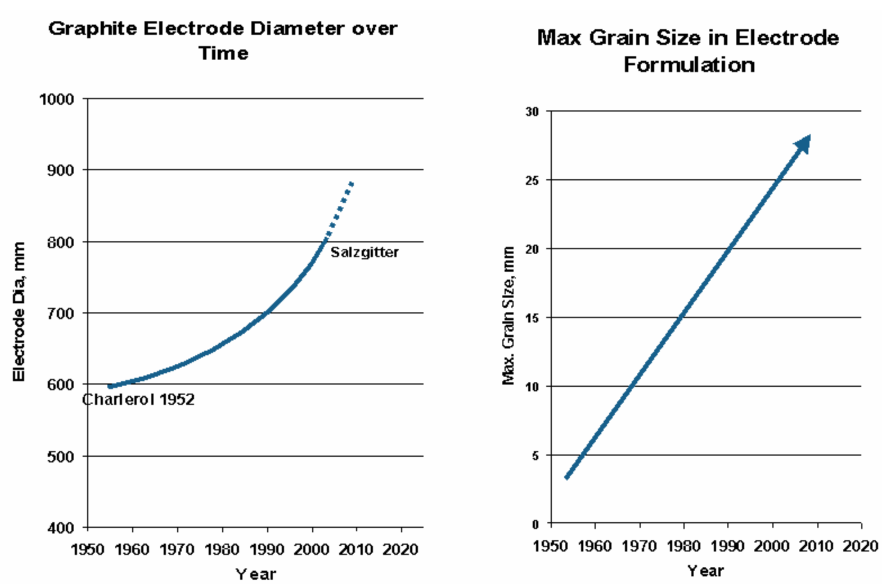


Fig. 12 Development of graphite electrode diameter and maximum grain size

To meet these coke grain size requirements, significant increase in the amount of grains greater than ½” was required. Figure 13 shows the improvement in the amount of these grains over time.

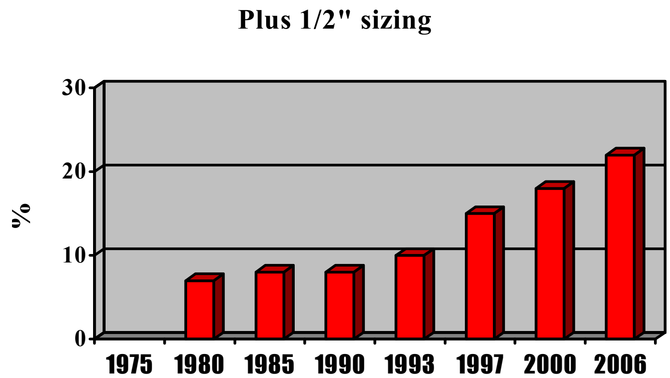


Fig. 13 Amount of coke grains greater than ½” in size

Acheson-type graphitization of GE was extremely energy intensive and therefore costly, but was necessary to manage previously poor coke qualities with high sulfur and nitrogen content. Although invented earlier, the more economic Castner, or so called lengthwise graphitization (LWG), was not applicable until the development of electrical rectifiers for these high currents. As these became available and needle coke with low sulfur and nitrogen was invented, LWG graphitization became the standard in the Western World for GE production. SGL Group’s plant in Italy (Ascoli) was the first to produce GE with the Castner process beginning in the 1960s.

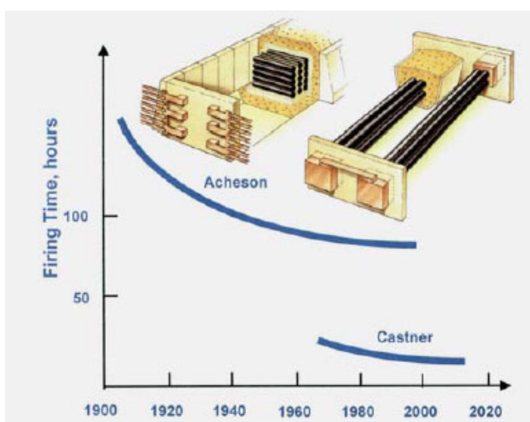


Fig. 14 Graphitization Technologies

The addition of iron-oxide as an inhibitor to electrode puffing, irreversible expansion, further reduced graphitization firing times to below 10 hours (fig. 14).
Since the early 1970s, needle coke qualities have further improved in their most important characteristics (fig. 15).

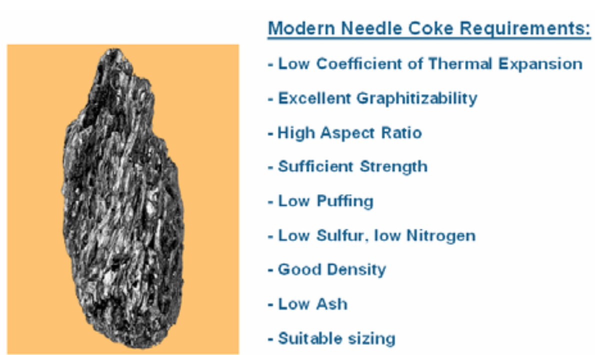


Fig. 15 Key quality properties for needle coke

In particular, significant improvement in the most important quality metric, coke CTE, is shown over the past 30 years (fig. 16).

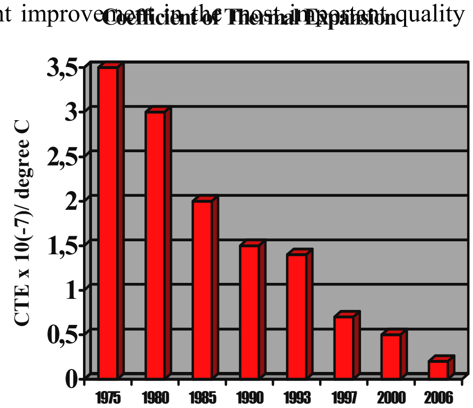


Fig. 16 Coke CTE improvement over past 30 years

Typical physical properties of today's graphite electrodes are summarized in fig 17.

Diameter	mm inch	350 - 450 14 - 18	500 - 650 20 - 26	700 - 800 28 - 32
Apparent Density	g/cm^3	1.60 - 1.75	1.67 - 1.77	1.68 - 1.77
Specific Electrical Resistance	Ωμm	5.0 - 7.5	4.5 - 5.5	4.0 - 5.5
Flexural Strength	N/mm^2	8 - 13	10 - 13	10 - 13
Thermal Conductivity	W/(K·m)	220 - 270	250 - 280	250 - 300
Coefficient of Thermal Expansion	μm/(K·m)	0.5 - 1.1	0.3 - 0.6	0.3 - 0.6

All values measured parallel to extrusion direction.

Fig. 17 Typical properties of graphite electrodes

Outlook

High energy prices and global competition will force mini mills to further improve the efficiency of steel melting. Furnaces with productivity below 75 t/h will likely disappear by 2010 (fig. 18). The focus will be on energy concentration. The share of chemical energy used will increase. Furnaces will be equipped with larger numbers of burners and lances to feed natural gas, carbon and oxygen more efficiently. Post combustion of CO in the furnace will also add to improved energy usage. The whole furnace system will be tighter to minimize heat losses. Therefore the thermal stress for graphite electrodes will increase, accompanied by an enhanced oxidation.

Global warming discussion on CO_2 release and its taxation might add some constraints, particularly locally. Electricity from nuclear power plants might become more cost attractive in future and re-favor the electrical energy input. However, as far as the future can be predicted, there is no competitive alternative to the EAF technology visible in the horizon.

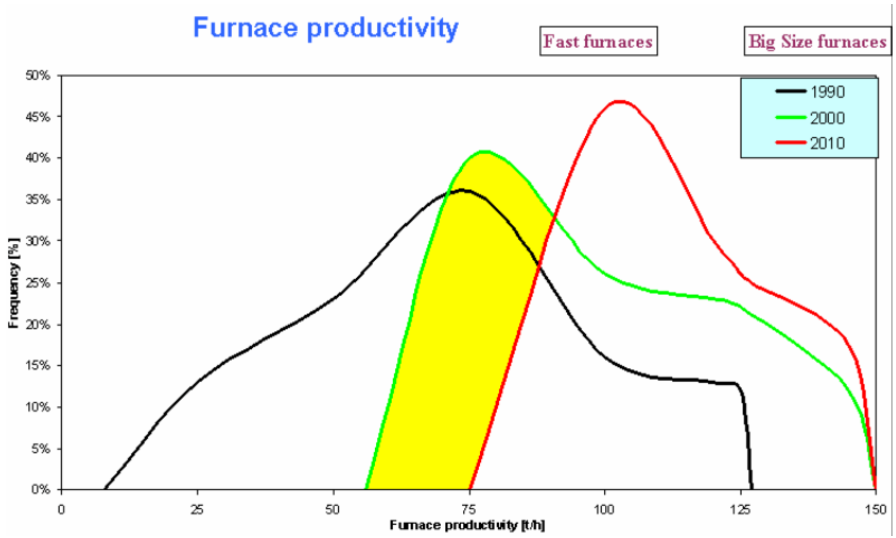


Fig. 18 Expected development in furnace productivity

It is obvious that our customers expect GE operating at maximum reliability and minimum consumption. This can be achieved by improving the raw materials and the process technology in Coke and in GE production.

The future of needle coking will focus on continuing the environmental improvements of the recent past. In addition, a strong emphasis on implementing some best practices from our fuel coking technology around worker ergonomics and safety improvements will be undertaken. This includes such items as autoheading of the coke drums to reduce cumulative trauma syndrome and remote unheading to remove workers from the vicinity of potentially dangerous areas during operations.

We feel strongly that continued participation in the high severity end of the needle coke market will require further coke and electrode quality improvements that we are currently working on. This quality improvement must come not at the expense of but in addition to further improvements in coker and electrode production economics.

The SGL Group - The Carbon Company – and ConocoPhillips Company cooperate with their key raw material suppliers to utilize the raw material quality required by the steel market today and to jointly develop the qualities for tomorrow. Basic scientific questions are addressed to specialized universities and institutes, as well as internal research facilities.

References

1. C. Friedrich, H. Jäger, K. Wimmer, C. Hauswirth, H. Fuchs, H. Schäfer, The world´s first 800 mm diameter graphite electrode for a DC electric arc furnace, Metallurgical Plant and Technology, MPT, 2., 2002
2. W. Frohs, Optimization of graphite electrode columns for electric arc furnaces, Metallurgical Plant and Technology, MPT 2, 1999
3. H. Hagel, A. Kruppa, K. P. Michels, H. Jäger, K. Wimmer, R. D. Klein, I. W. Gazda, Thermal induced stress situations of graphite electrodes in DC- arc-furnaces, Proc. 21st Biennal Conf. on Carbon, 1993 Buffalo, p 727/28
4. Ullmann`s Encyclopedia of Industrial Chemistry, Chapter Graphite, Industrial Carbon Wiley-VCH, Edition 2007, in preparation
5. C. Friedrich, H. Fuchs, Selecting the optimum electrode diameter for AC EAFs, MPT 5, 2005