POTENTIALITIES IN THE PASTE PLANT

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Abstract

Much of the progress made recently in paste plant technology has come from computerized process control, improved process philosophy and P & ID's as well as full level 2 operation. This paper will focus on materials aspects to get out more from the intrinsic properties of coke and pitch. Proposals will be made how to utilize in a better way the structural properties of petroleum coke and the fluid and carbonization properties of binder pitch. Potential changes in equipment and lay-out will also be discussed.

Introduction

Over the last decade much progress has been made in the paste plant through the implementation of computer systems for process information and process control. The various process groups are interlocked and for most of the operating time the computerised paste plant runs smoothly and steadily in automatic mode. As displayed in Figure 1, today's paste plants may not only differ in their technology principles and key equipment, but also in the spectrum of pro cess group philosophies, process and information

1.8 Quality control

1.7 Job steps & CBP's

1.6 PLC Diagrams

1.5 P & I Diagrams

1.4 Control philosophy

1.3 Key equipment

1.2 Process group philosophy

1.1 Technology principles

2.8 Quality control

2.7 Job steps & CBP's

2.6 PLC Diagrams

2.5 P & I Diagrams

2.4 Control philosophy

2.3 Key equipment

2.2 Process group philosophy
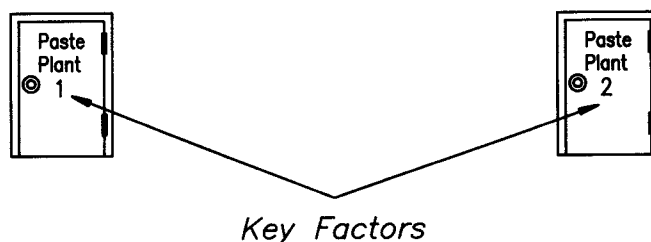
2.1 Technology principles

Figure 1: Main Characteristic Items of Paste Plant Technologies

diagrams (PID's), set points and finally in the applied software. There is still some room for further improvement and the optimisation of minor process steps by means of sophisticated computer programs. It is, however, believed that technological leaps or major advances cannot be expected anymore from intensified computerisation. For this reason, one has to look again at other aspects of process technology, namely materials and equipment.

The main objective of this paper is to pursue the idea of whether we can get more out of the inherent properties of calcined petroleum coke and electrode pitch to the advantage of green anode blocks and their subsequent treatment. In connection with all the aforementioned measures to ameliorate technical procedures, the key management question must always be whether such developments pay off or are economically convincing.

Better utilisation of petroleum coke properties

The structural characteristics of calcined coke play a predominant role in the paste plant. Table I gives a simplified example of how specific coke properties can be allocated to the consecutive areas of anode manufacture and consumption. The most common structural properties, which can be determined in petroleum coke, are listed in Table II. Many of these structural features vary with particle size, examples for two types of petroleum coke are shown in Table III.

In the dry line of the paste plant, most of our effort is dedicated to the preparation of particle fractions by crushing, screening and grinding, and to the proportioning of such particle fractions to give an optimised dry aggregate. This means that the particle size is the prevailing factor.

If one takes a closer look at the individual particles of a definite, tightly screened size population, essential differences will be discovered among the particles with respect to strength and total porosity.

When taking, for instance, a coarse particle fraction of above 8 mm, some big particles can be easily broken between the fingers, whilst others are stronger and withstand this manual crushing force. Particle stability, therefore can be utilised as

Table I: Some Effects of Coke Properties

Area	Coke property	Effect on
In the paste plant	Particle size distribution Real density Particle porosity (total) Particle stability	Maintaining the desired recipe Apparent density of the anode Apparent density of the anode Degradation of coke particle size
In the baking furnace	Sulfur	Formation of sulfides Fe->FeS, Ni->NiS Na->Na$_2$S, Si->SiS
In the cell after anode change	Coefficient of thermal expansion (CTE)	
In the electrolytic cell during cycle time	Metallic V impurities: Na Fe Ca Sulfur	Air reactivity Air and CO$_2$ reactivity Air and CO$_2$ reactivity CO$_2$ reactivity Environment due to SO$_2$

a criterion of selection. The technological problem to be solved implies the separation of strong particles from very weak and fragile ones, i. e. the coarse and strong particles have to be preserved and retained for the coarse particle fraction, while the friable particles have to be crushed and directed to the medium or fine fractions. Conventional roll or hammer mills, however, do not have a selective crushing capacity. Impact crushers may even preferentially smash the dense and strong grains. One of the mechanical solutions to this selection problem may consist of employing a rubber-lined double-roll crusher. The edges of the strong and structurally sound particles will thus sink into the rubber surface and slip unaffected through the gap between the rolls; in contrast the friable particles, which contain predetermined fissures from their abrupt shrinkage during calcination, will be split apart and broken down.
Figure 2 illustrates the simple mechanism of selectivity.

Total particle porosity is the other important coke property which is considered to be worthy of an extra selective process step. The target is simply to separate the dense and less porous particles from those which are highly porous. The heavy low-porosity particles will be conveyed to the

Table II: Structural Properties of Petroleum Coke

No.	Property	Determination	Important aspect
1	Particle size distribution	Sieving analysis on representative samples with set of sieves	Selection of sieve series and of sieve apertures. Type of sieving machine
2	Particle size distribution of powder or dust	a) Special sieving b) Laser granulometry c) Blaine surface area d) BET surface area	Reliability and comparability of the methods
3	Particle shape	Particular methods, not used in routine control	Shape factor: Irregular, rounded, splintery, needle-like, As a function of particle size
4	Apparent particle density (AD)	a) Mercury displacement b) Water displacement (VAW)	Toxicity of mercury As a function of particle size
5	Particle porosity (Total, open, closed)	Total porosity from RD and AD (VAW method)	As a function of particle size
6	Bulk density	Loosely poured into volumetric vessels	On particle fractions. Design factor for silos and bins
7	Tamped (vibrated) bulk density	Maximum packing density by tamping or vibrating	As a function of particle size
8	"Swimming" coke	Floating particles in water, skimmed off from the surface	Light and spongy portions Method used for entry control
9	Real density (RD)	On powdery sample (<0.063um) a) Xylene method b) He comparison c) X-ray diffraction -> L_C	On average sample. As a function of particle size
10	Particle stability	a) AKK method (Vibrating mill) b) VAW method (Turbulent mixer)	Not only on standard particle fraction of 4 - 8 mm, also on 2-4, 1-2, 0.5-1 mm
11	Grindability	a) Hardgrove test b) VAW: Vibrating rod mill test	Sample as feed material for ball mill

Table III: Test Results of some Structural Coke Properties

	Sieve fraction mm	Pro-portion %	Bulk density g/cm3	Tamping density g/cm3	Apparent density g/cm3	Real density g/cm3	Total porosity %	Stability % AKK	Stability % VAW
Coke Type I	<0.5	12.0				2.080			
	0.5 - 1.0	16.0	0.77	0.89	1.86	2.082	10.7	54	91
	1.0 - 2.0	20.7	0.75	0.89	1.85	2.086	11.2	56	87
	2.0 - 4.0	17.6	0.69	0.70	1.80	2.088	13.7	59	74
	4.0 - 8.0	13.9	0.63	0.70	1.73	2.089	17.1	73	68
	8.0 - 11.2	6.6	0.57	0.61	1.68	2.095	20.9	73	65
	>11.2	13.2				2.100			
Coke Type II	<0.5	8.8				2.037			
	0.5 - 1.0	15.0	0.70	0.89	1.77	2.039	13.1		
	1.0 - 2.0	18.6	0.64	0.77	1.73	2.054	16.0	52	86
	2.0 - 4.0	15.7	0.61	0.71	1.69	2.062	17.9	51	56
	4.0 - 8.0	18.5	0.57	0.67	1.66	2.059	19.6	63	61
	8.0 - 11.2	10.9	0.53	0.61	1.62	2.063	21.6		
	>11.2	12.5				2.066			

fraction bins, whilst the light high-porosity particles will be diverted to the ball mill circuit for grinding to a fine powder.

An analogous process may be mentioned here. When carbon lining blocks are manufactured from a mixture of fairly dense, gas-calcined anthracite and extremely porous metallurgical coke, it is a well-known fact that the dense anthracite is used for the coarse and medium particle fractions and the quite porous metallurgical coke for the fine and dust fractions.

The different individual porosities of coke particles, obtained from a narrow sieving range, can readily be demonstrated by carrying out a sedimentation test in water. The majority of particles will fall and settle fairly quickly, but a sizeable portion of particles will exhibit a comparatively low velocity of fall or will even remain floating on top of the water surface, despite the addition of a wetting reagent. The differences in single particle porosity are very distinct in the size range 0.5 to 4 mm, and less pronounced for coarser particles above 8 mm, although these coarse coke particles show on average a significantly higher porosity (see Table III).
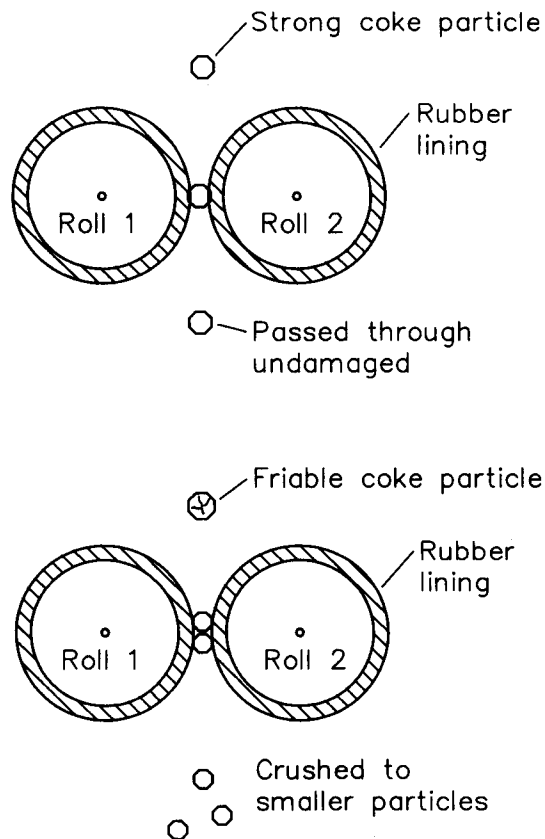

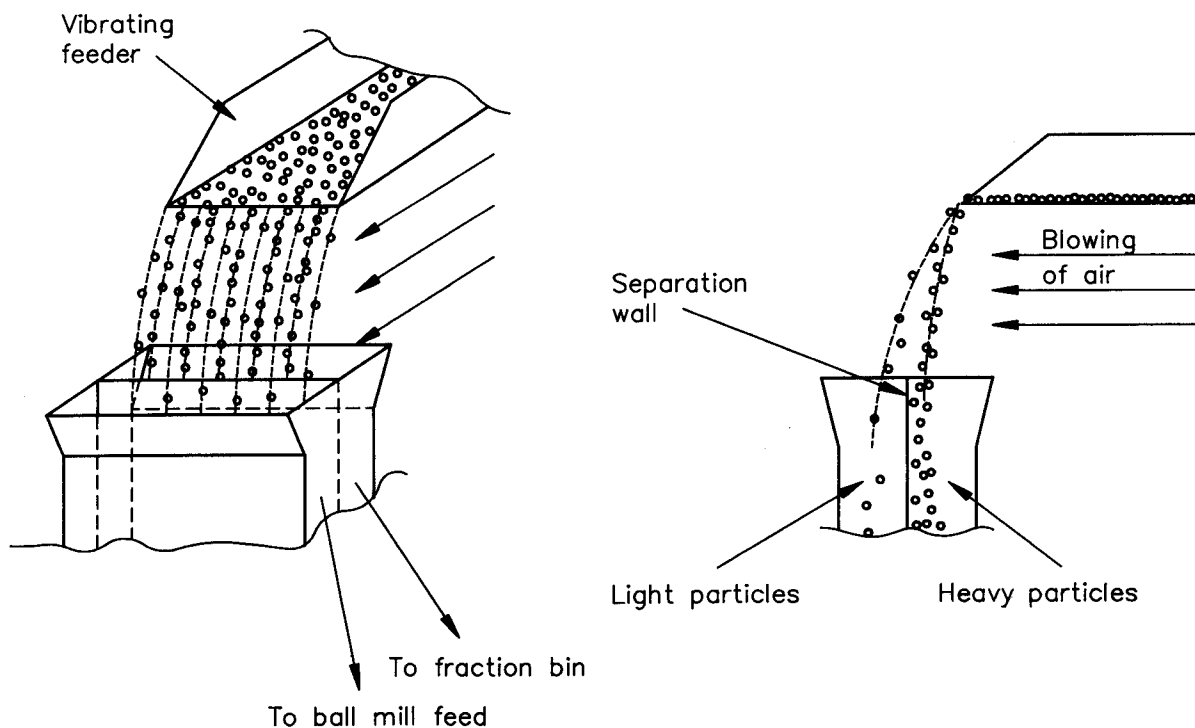Figure 2: Selective Crushing of Coke Particles

Figure 3: Principle of Seperating Light and Highly Porous Particles from Heavy and Dense Ones

The separation of the light, high-porosity coke particles from the heavy, low-porosity particles can be achieved by blowing a stream of air through a thin falling curtain of a finely screened particle fraction. The principle of such a separating device is sketched in Figure 3. A curtain of particles running down a cascade with louvers may enhance the separation effect.

Now, quite justifiably, the question has to be asked: "What kind of benefit may be gained from this?" Stronger and more compact particles are accumulated in the coarse and medium fractions. Assuming the same original recipe, a higher apparent density with favourable effects on strength, permeability and resistivity can be achieved. This is obtained without the risk of generating more baking scrap or creating a higher sensitivity to thermal shock cracking. The increase in baked apparent density may be exploited by planning a longer cycle time of the anodes in the pot. Alternatively, one may also formulate a coarser composition of the dry aggregate with a lower proportion of fines and hence a reduced content of pitch in the green mix or paste. If the pitch in the green scrap is included, one may attain a total pitch content as low as 13%.

Table IV:

Evaluation of Electrode Pitches

Area	Property	Operational Parameters of Impact or Effect
In the paste plant	Softening point Viscosity Wetting capacity Change in density (Thermal expansion)	Level of processing temperatures during mixing and forming Crack formation on cooling
In the baking process	Distillation loss Coking value Strength of carbon bond (Toluene and quinoline insolubles) Reactivity of binder coke	Heating rate during carbonization Final heat-treatment temperature
In the electro-lytic cell	Residue and type of binder coke Degree of calcination Catalytic elements such as Na, Ca, Fe	Disintegration of bond structure Dust formation Burn-off rate

Better utilisation of pitch properties

Viscosity is the outstanding fluid property of pitch which is of prime interest in the paste plant. The mixing and forming temperatures primarily depend on the pitch viscosity, which is closely related to the softening point. The other characterising properties of pitch are more relevant in downstream areas such as cooling, baking and consumption of the green or baked anode, respectively, (see Table IV).

In the traditional temperature ranges of pitch handling, mixing and forming, up to 250 °C maximum, the viscosity of electrode pitches decreases exponentially with temperature. The softening point is generally taken as the reference parameter. The viscosity-temperature graphs of pitches, having different softening points, will normally run almost parallel to one another (see Figure 4). It is very interesting to know how the viscosity functions continue at more elevated temperatures, for instance, between 250 and 450°C. It can be stated that the viscosities of coal tar pitches reach a minimum, before they undergo distillation, mesophase formation, pyrolysis and finally carbonisation. The latter conversion phases are associated with a steep increase in viscosity (see Figure 5). It is difficult to perform reliable viscosity measurements in the minimum range because these measurements may be disturbed greatly by the phenomena of pitch volatilisation and distillation, both of which lead to a more viscous melt. As a result, the viscosity values are influenced by the duration and conditions of measurement. It was also verified that high-softening pitches never reach the low-viscosity levels.
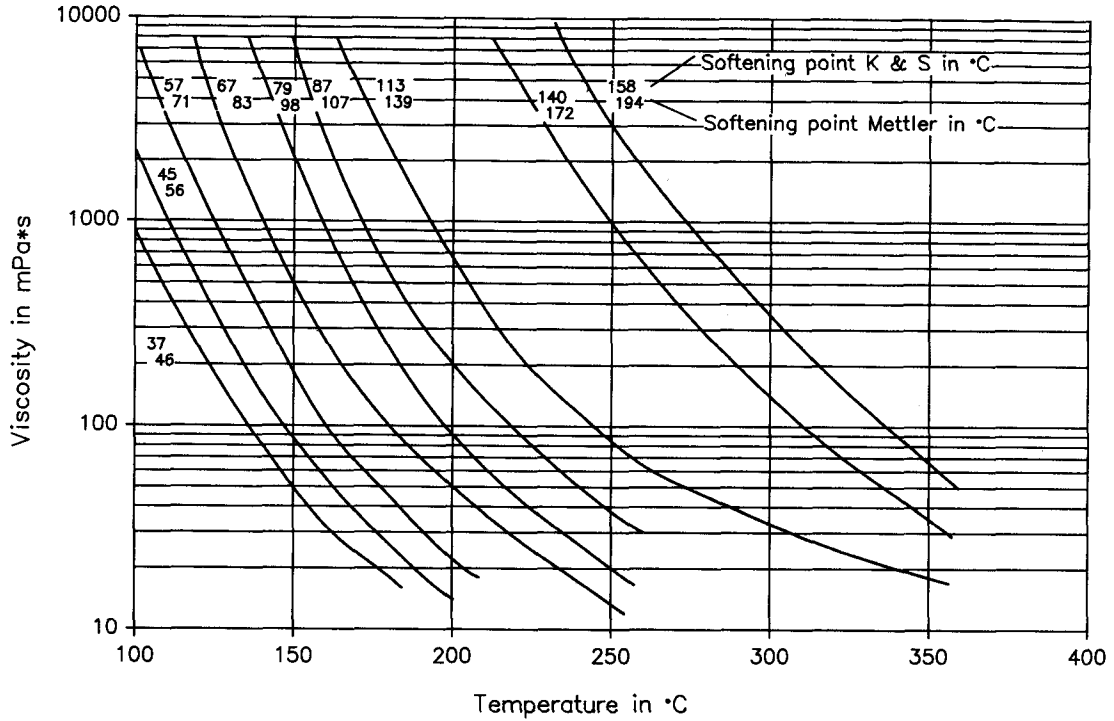
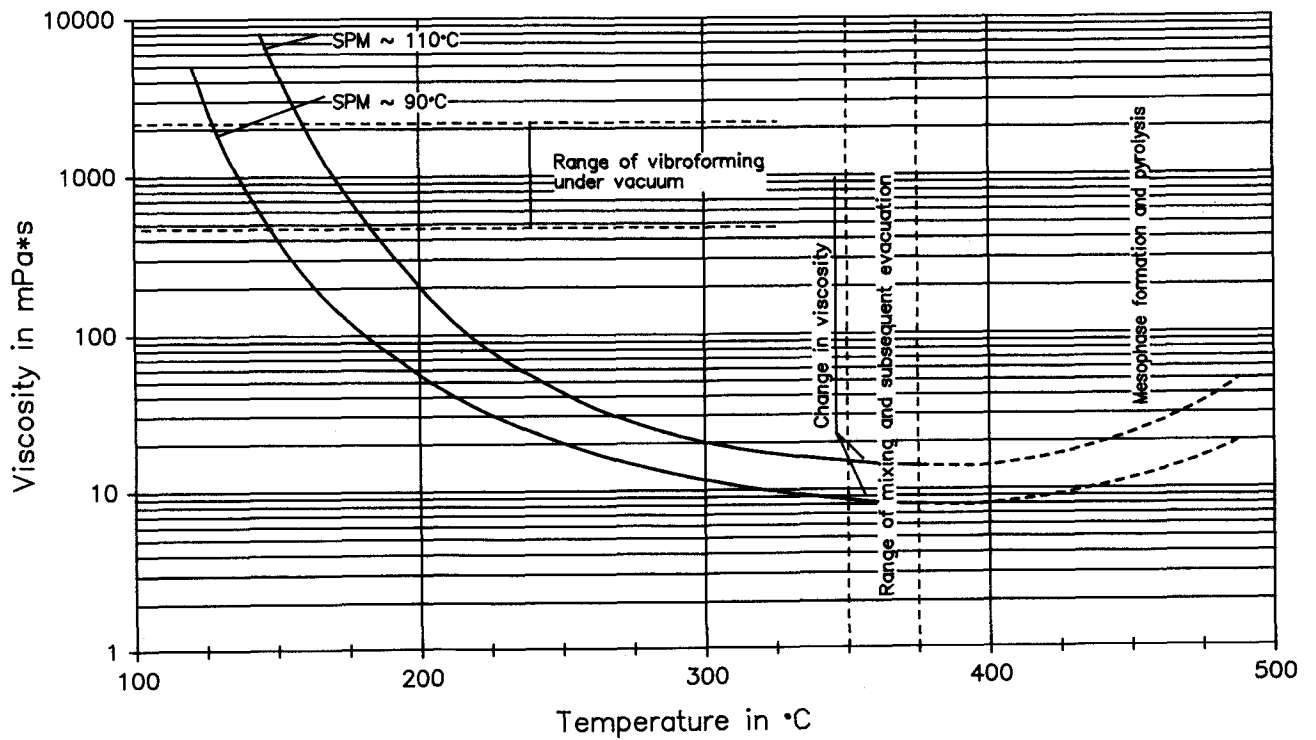**Figure 4: Viscosity of Pitches of Different Softening Points**

Figure 5: Viscosity of Pitches as a Function of Temperature up to Elevated Temperatures

On the basis of the above information about pitch viscosity as a function of temperature, a quite novel process has been conceived. It is outlined in Figure 6.

The dry aggregate is electrically preheated to preferably 350 - 400°C, the liquid pitch to around 350°C. Very little mixing power is needed to intimately combine the solid and liquid components. Adsorbed moisture and air are largely scavenged from the carbon dust surface at temperature levels above 300°C. In addition, the wetting capability of the fuming pitch at viscosities far below 100 mPa • s is enormous. If the conventional type of continuous kneader is chosen for mixing, it can be operated at significantly higher rotation speeds, and be designed with a much smaller capacity compared to a standard mixing process at operating temperatures of 160 to 190°C. Furthermore, an alternative type of mixer may be devised.

After mixing, the extraordinarily hot paste is subjected to a vacuum treatment during which the green mix should gently be agitated. Due to the extremely large surface area of the pitch coating on the dry aggregate, the low-boiling constituents and light volatiles are rapidly evaporated from the pitch films. About 15% of the pitch is distilled off. The viscosity increases by a factor of almost one hundred. At the same time, a substantial amount of heat is extracted from the paste causing its temperature to drop slightly. The vacuum treatment may either be carried out batch-wise with two vessels charged and discharged alternately, or in a continuously operating apparatus.

The green tough mix is vibro-formed under vacuum at temperatures of at least 250 °C.

According to the proposition above, this modified process group of the paste plant combines three substeps in line which may be briefly described by the following headings:

- mixing at minimum viscositiy,
- high-temperature treatment under vacuum,
- super-hot vibroforming under vacuum.

The fundamentals of this process have been studied and tested successfully on laboratory scale.
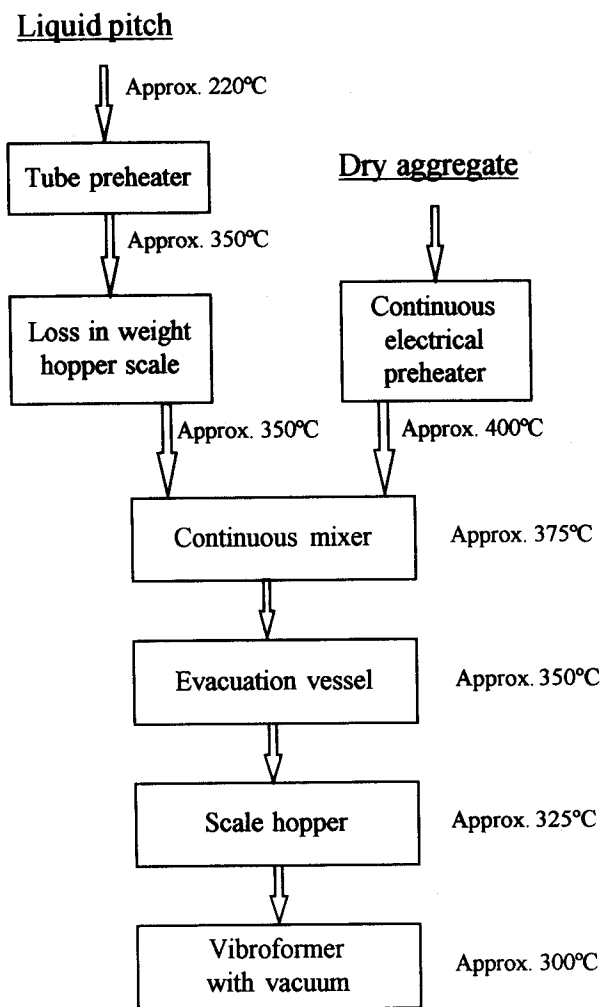

Figure 6: Novel Green Line in the Paste Plant

At the end of this section, one may ask again a pertinent question: "How much can be saved on investment and operating costs by adopting such an unusual and hot system?" It seems that the high operating temperatures pose no problem. Such temperature levels are regarded as being quite normal in the petrochemicals and plastics industry for similar equipment. Capital expenditure and operating costs for the vacuum treatment unit handling the paste after the mixer are assumed to be about equal to those for a cooling mixer installed in some paste plants.

The first advantage which will result from the foregoing process is a change in anode cooling. It is believed that water cooling as spray or immersion cooling can be abandoned. The super-hot-formed anodes can be cooled sufficiently in air. They are already quite stable when released from the mould, and their forming temperature is far above the ambient temperature.

An amazingly high carbon yield of 85% was found for the pitch in baked bodies which were made of the vacuum-treated and super-hot-formed paste. Mechanical strength and electrical resistivity were excellent. These findings lend hope to the supposition that this special type of green anode can be baked with increased heating and throughput rates.

Green anodes produced using the described method may be suitable for continuous green anode stacks in electrolytic cells and for the replacement of monolithic Soederberg anodes. The loss of total volatile matter can be reduced to below 2.5%. Stub holes can be drilled into the green blocks or a continuous sliding contact may be provided by a kind of granular graphite stuffing box. The substitution of Soederberg paste by the low-volatile preformed anode blocks is based on the fact that these anodes are fairly self-supporting in their transition phase to coking at elevated temperatures.

Conclusions

Both, petroleum coke and pitch offer chances of improvements in the paste plant, which are not limited to the paste plant itself but may have favourable impacts on subsequent production areas.
With regard to coke, selective procedures can be introduced to preserve and retain the strong particles and to crush the friable particles selectively as well as to separate light and very porous particles from heavier and less porous ones.

The potential for enhancing the utilisation of pitch lies in three basic areas: in the application of mixing temperatures close to the material's viscosity minimum, in a high-temperature vacuum treatment of the paste to remove excess volatiles from the pitch, and in a super-hot vibroforming under vacuum.
Green anode blocks manufactured using these new process steps may also be used in Soederberg cells as continuously glued blocks instead of Soederberg paste.