New developments in battery oxide production

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Abstract

This paper is presented in two parts. The first deals with a detailed analysis of battery oxides produced by several Barton-pot and ball-mill plants. The data are used in a critique of the various product-quality measurements currently in use. The second part of the paper discusses developments carried out by Heubach & Lindgens Engineering in oxide quality, operating costs and environmental performance.

Structure and quality criteria for battery oxides

The two processes for battery oxide production, namely, the Barton-pot and the ball-mill processes, give rise to products with very different structures. This is not surprising given the very different methods of lead dosing, i.e., as a liquid in the Barton-pot and as a solid in the ball-mill counterpart. The detailed structure of battery oxide is best examined by electron microscopy. Two sample preparation techniques are appropriate to enable the different oxides to be judged optimally: (i) untreated product; (ii) slices taken from a sample mounted in resin.

Figure 1 displays electron micrographs of nine oxide samples each obtained from different production plants. Four of the samples (B1 to B4) were obtained from Barton-pot units and five (M1 to M5) from mill plants. The Barton samples all appear to have a relatively regular crystalline structure whilst the mill samples appear to be irregular.

When mounted in resin and polished in cross section, the samples of Fig. 1 display a very different picture when electron micrographs are obtained at the same resolution (Fig. 2). For the Barton oxides, the metallic free lead, which was not visible with the simple product micrographs of Fig. 1, now appears in the form of large particles formed from solidified lead droplets. By comparison, the oxide consists of much smaller, more regularly formed particles. Combinations, or large agglomerations, of the two phases appear to be a rare occurrence. With the mill oxide, on the other hand, fairly large agglomerations can be observed. These have small, bent slices of lead at their centres. The micrographs demonstrate this effect in various forms that are dependent upon the orientation of the particle. The surrounding oxide particles are of a far greater fineness — much finer than the Barton oxide — which is explained by the well-known grinding effect of the ball-mill process. A good overview of the structure of the nine samples is given in Fig. 3 which was prepared at a lower magnification than Fig. 2.

Which quality criteria can be used to describe the heterogeneous and complex structure of battery oxide? In the following text, a series of physical and chemical measurement techniques are described and critically evaluated. Table 1 provides an overview summary of these tests on the nine samples.

TABLE 1.

Analytical results for battery oxides

Measurements	Oxide type								
	B1	B2	B3	B4	M1	M2	M3	M4	M5
Metallic lead, Pb (wt.%)	28.8	26.6	28.8	25.4	33.8	31.8	36.8	27.4	30.5
Oxide content, PbO (wt.%)	71.1	73.4	71.2	74.5	66.1	68.1	63.2	72.6	69.5
Absorption H_2SO_4 (‰)[a]									
1	196	182	207	221	254	232	232	281	265
2	176	167	174	190	243	212	225	267	271
3	153	135	147	173	230	192	224	254	256
Paste torque (N cm)	130	102	129	167	148	59	126	123	157
Specific surface area									
BET ($m^2 g^{-1}$)	0.8	0.9	0.7	0.9	1.5	1.3	1.8	1.8	2.1
Kozeny–Carman ($m^2 g^{-1}$)	0.8	0.8	1.0	0.9	1.8	1.1	1.5	1.8	2.3
Scott density (g ml^{-1})	1.3	1.6	1.3	1.4	1.2	1.6	1.8	1.3	1.4
Tamped density (g ml^{-1})	3.6	3.9	3.5	3.5	2.9	3.7	3.5	3.2	3.0
Sieve residue 63 μm (%)	0.2	0.6	1.4	0.07	0.7	1.2	4.0	2.5	4.1
Sieve residue 32 μm (%)	2.4	2.2	3.5	0.2	2.7	7.4	22.9	10.3	11.4
Particle size D_{50}									
Coulter counter (μm)	3.3	3.8	3.5	3.0	4.2	2.6	6.4	3.7	7.8
Sedigraph (μm)	3.4	3.3	2.8	2.5	3.2	2.2	6.8	2.0	2.8
Mastersizer I (μm)	5.5	5.3	5.5	4.2	7.7	3.1	17.4	6.8	12.7
Mastersizer II (μm)	5.5	5.4	4.3	3.5	6.6	4.9	8.3	7.2	5.0
Microtrac I (μm)	5.3	5.0	4.9	4.0	6.5	4.2	12.0	5.6	8.3
Microtrac II (μm)	5.7	5.2	5.2	3.9	8.2	4.3	13.9	6.5	9.3

[a]‰ = mg H_2SO_4/g oxide.

Free-lead content

This measure is very important for oxide manufacture and needs to be precisely adjusted by the oxide producer and controlled with minimum deviations from the set point. The value can be determined in two ways: the oxide is dissolved in acetic acid and either the remaining undissolved lead is separated and weighed or the oxide content is measured directly by titration. Both techniques give the same end result although the weighing of the lead residue must be carried out particularly carefully.

Acid absorption

The only chemical analysis directly applicable to battery oxide is the above-mentioned measurement of free lead. Various impurities in the oxide, e.g., iron, can also be measured by this method. A further characteristic that is dependent upon the fineness of the product is the sulfuric acid absorption capacity. This is the second pure chemical measurement. The test is carried out by most oxide producers and users and, in general, the highest possible value is desired. It must be stated that the measurement result is strongly dependent upon the analysis procedure and requires well-trained laboratory staff. Table 1 shows the degree of variation for samples analysed according to various prescribed methods. An internationally agreed standard for the determination of oxide acid absorption is a worthwhile aim.

Paste torque

The reaction of the oxide with sulfuric acid — two of the components that go to make up the paste — shows that the paste consistency is dependent upon the oxide. The measure is considered by some users as an indication of oxide quality. The consistency is measured by the so called 'paste torque' in which the torque required to knead a given mass is measured in a special apparatus. The paste torque, which
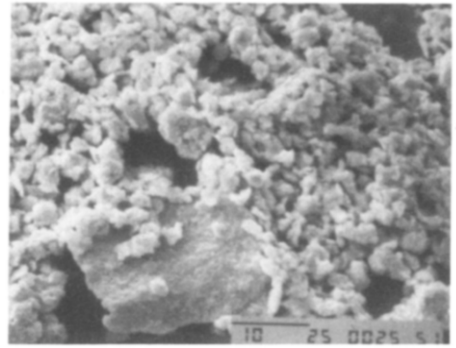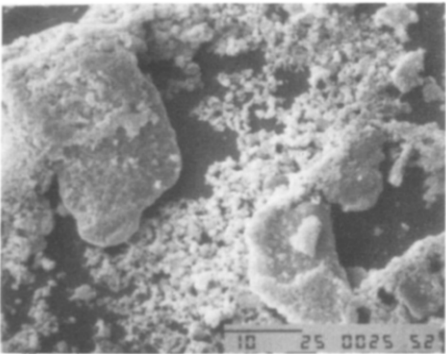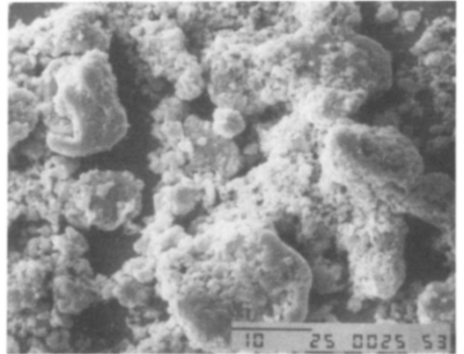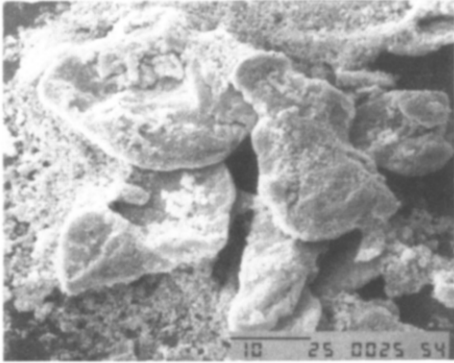
B1

B2
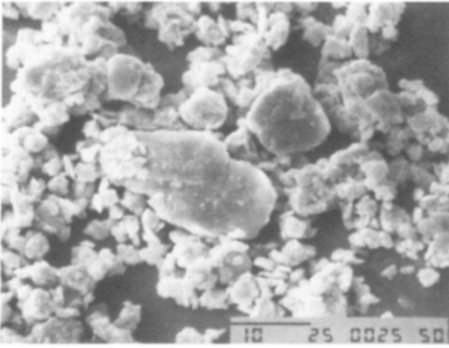
B3

B4

M1

M2

Fig. 1.   (*continued*)

M3
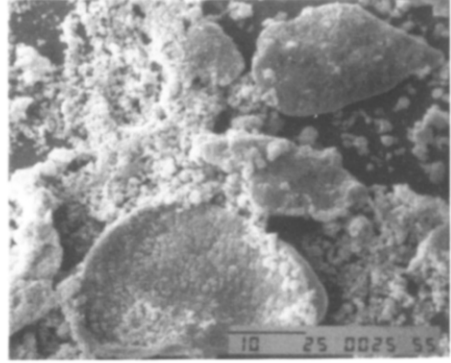
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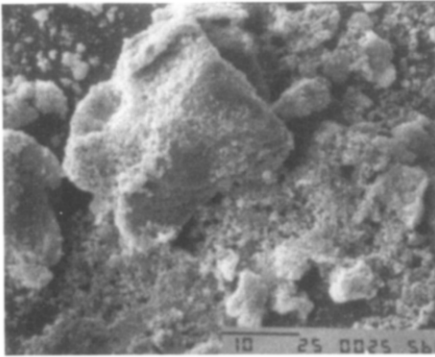
M5

Fig. 1. Electron micrographs of four Barton-pot (B1 to B4) and five ball-mill (M1 to M5) oxides.

is partly related to the acid absorption, is a practical measure and a high value is desired.

Water take-up, penetration

The consistency of paste formed only with water is also used by some battery producers as a criterion for oxide quality. The measurement is carried out by the following process: a paste is formed between the oxide and water with the latter being added until a falling cone-shaped weight penetrates a given distance into the paste. The amount of water added is then given as the 'water take-up' in units of per thousand.

Specific surface area

The ability of the oxide to react with sulfuric acid depends much upon the specific surface area. This measurement is carried out by a pure physical method and provides a further specification for the oxide product. The BET procedure using liquid nitrogen produces the most accurate results, but is not really suitable for frequent and regular measurements. The Kozeny–Carman method (on which the Heubach Permeatron device is based) produces results comparable with the BET method together with the added advantages of being very quick and easy to determine. This enables the specific surface area to be considered as an important and accurate physical parameter of the oxide.

Density

From a practical viewpoint, the apparent density of the product is very important. It influences the density of the paste (described above), and, thereby, the amount of oxide in the battery. The oxide density can be measured by the Scott method in a specially designed apparatus, or as a tamped density (a much more meaningful value) again in a standardized device. The Scott and tamped densities of the nine samples
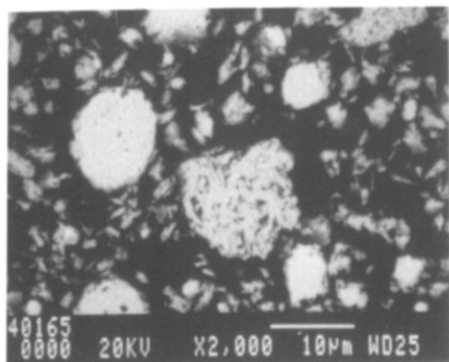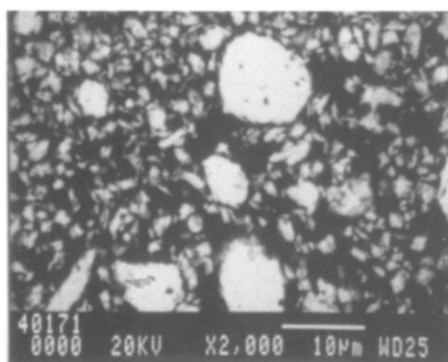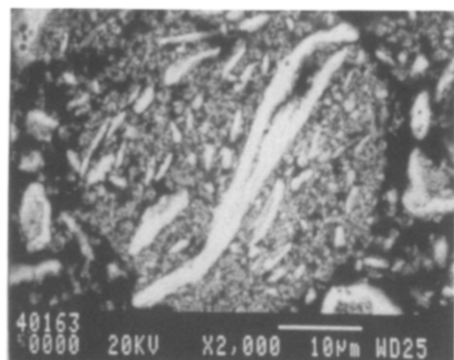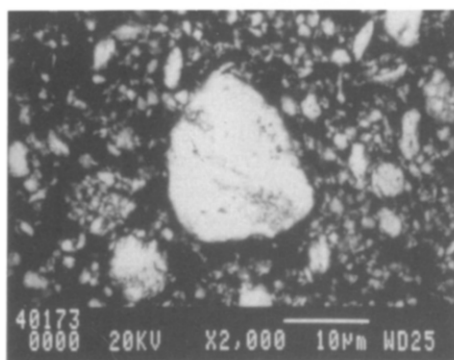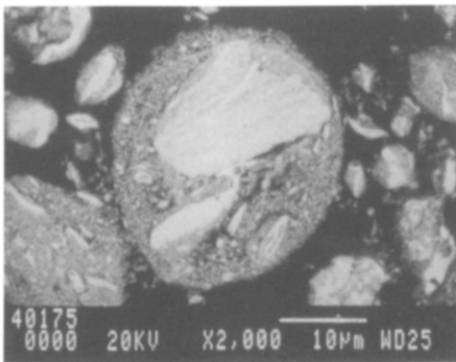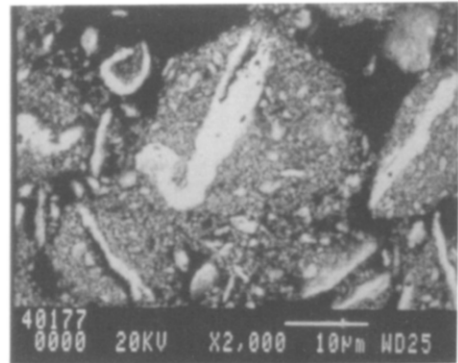

B1
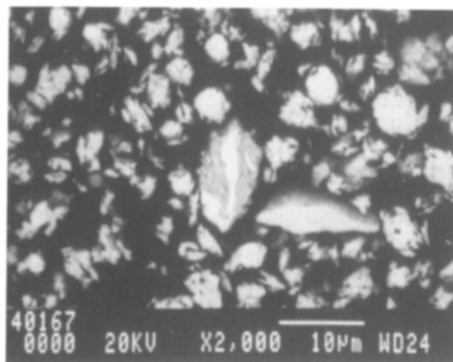
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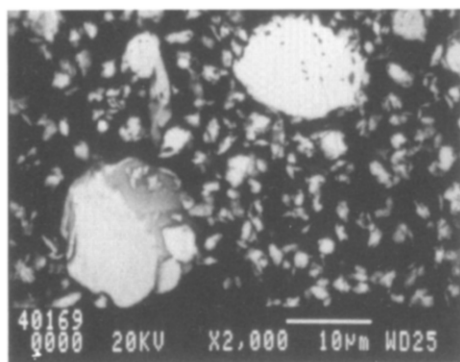
B3

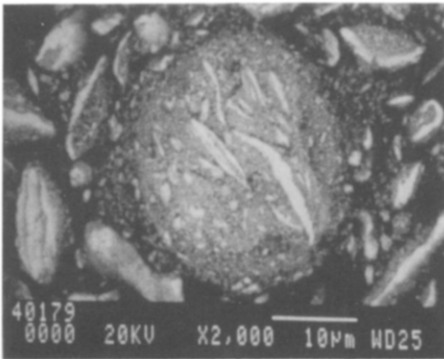B4

M1

M2

Fig. 2. *(continued)*

M3

M4

M5

Fig. 2. Electron micrographs of polished cross sections of the oxides shown in Fig. 1, and at the same resolution.

are also displayed in Table 1. For the sake of completeness, it should be mentioned that the real density of the heterogeneous oxide is ~ 10 g ml^{-1}.

Particle-size distribution

A particle spectrum analysis is commonly carried out as part of the characterization of the oxide. Table 1 shows the results obtained with the samples under consideration. The analyses were carried out using three different techniques, as follows:

(i) particle counter in a capilliary device (Coulter counter);
(ii) sedimentation (Sedigraph);
(iii) laser diffraction (Mastersizer and Microtrac).

Before the analysis, each sample has to be dispersed in a carrier fluid. The importance of the dispersion is shown by the results of the Mastersizer analyses. In this case, the first sample was not dispersed whilst the second was dispersed over a defined period using ultra-sound. The carrier fluid, itself, also influences the results, as demonstrated by the Microtrac analyses.

The above results show that it is clearly not possible to achieve agreed values. Thus, it is not possible to quote distribution curves, or mean particle sizes. The poor accuracy of the absolute results is shown by a comparison of the mean particle-size with that calculated from the BET surface area. The latter implies a mean particle-

size of 0.3 to 0.6 μm and this is almost an order of magnitude smaller than that calculated for the oxides by the three methods used.

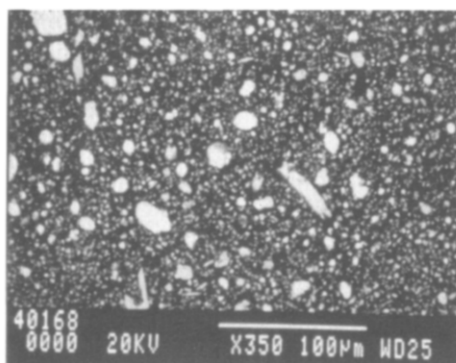When carrying out particle-size studies, it is not usually the overall distribution curve which is of interest, but rather the fraction of larger particles >63 or 32 μm (230 or 450 mesh) as measured by wet sieving. If the fraction of large particles is too high, then problems will occur in the pasting machines, especially on thin grids.
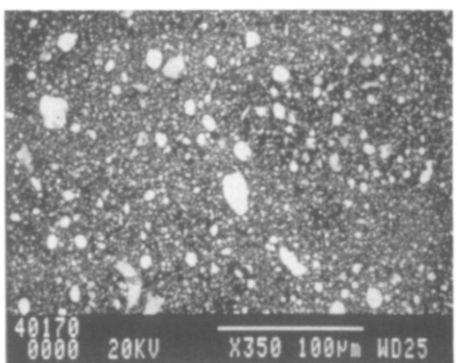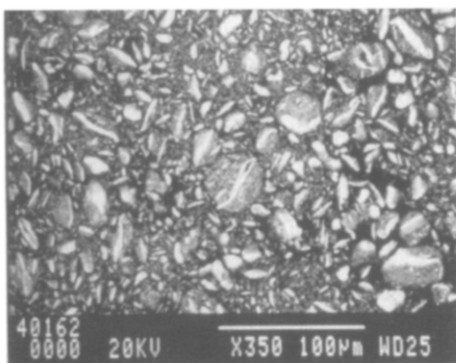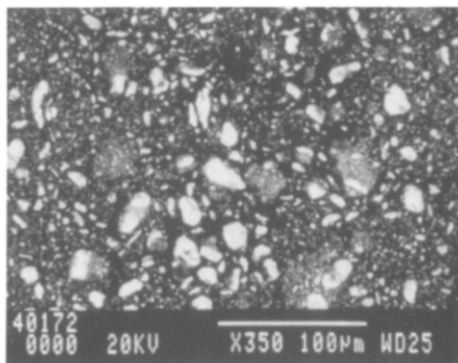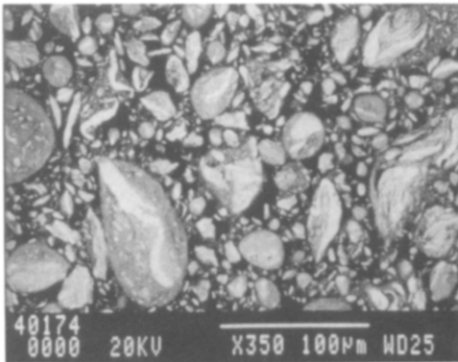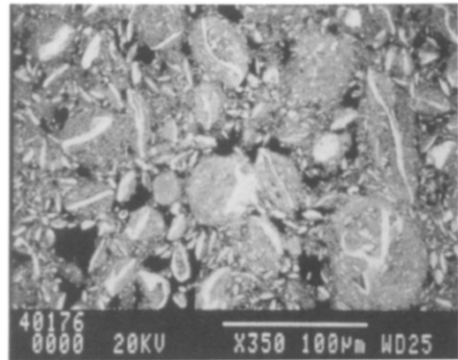

B1

B2

B3

B4

M1

Fig. 3.

M2

(*continued*)

82
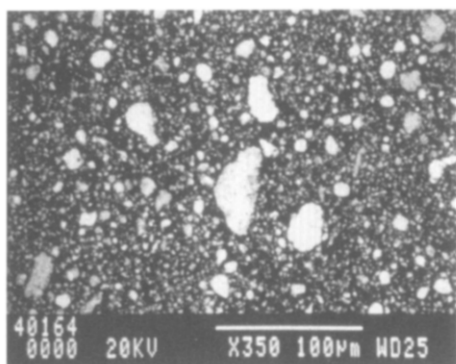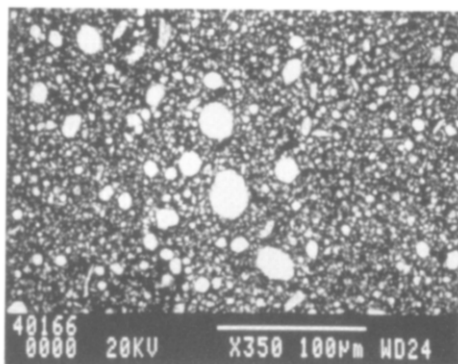
M3

M4
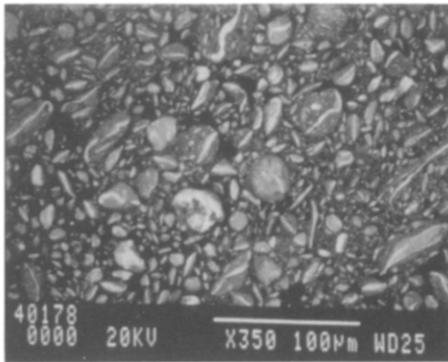
M5

Fig. 3. Electron micrographs of Fig. 2 at a lower magnification.

Crystalline structure

A battery oxide should consist to the highest possible degree of the alpha (or tetragonal) modification. This requirement is met by ball-mill oxide but Barton-pot oxides contain a small fraction of the beta (or rhombic) modification. The analysis itself can only be carried out by X-ray diffraction and, therefore, is not therefore suitable for routine tests.

Summary

The eight quality criteria outlined above enable a battery oxide to be closely defined. In normal practice, for routine production control, two or three methods at most can be considered — especially when the oxide is produced in the same plant. Again, it would be extremely useful if an international standard, or standards, could be agreed upon for the prescribed analytical methods.

Developments in battery oxide

There are a number of significant differences between the oxide produced by the Barton-pot and ball-mill processes. The authors' company, Heubach & Lindgens, has oxide production facilities in Germany of ~65 000 t/annum capacity and has conducted

considerable developmental work that has resulted in several patents in the lead oxide field.

The company's strategy of constant development is focused on three main areas:
- oxide quality
- production costs
- environmental performance

Oxide quality

The oxide product quality will be treated in two steps: general process developments followed by a separation system modification leading to a significant improvement in the Heubach Barton-pot oxide.

In process development, a major aim has been to build in a high degree of automation. This has led to a high degree of consistency and control over the main operating variables and, thus, the oxide quality. For both the Barton-pot and ball-mill processes, the major process parameters are the operating temperature and the mass hold-up or through-put. For the Barton-pot method, this means the liquid lead feed rate to the reactor and the reactor temperature. Control of the lead feed rate is achieved by having a good design for both the lead melter and the dosing pot. The aim is a constant lead dose rate with minimal manual intervention. The reactor temperature is held constant by varying the air-flow feed. Important features of the temperature control are the correct positioning of the measuring element and careful operation so as to avoid oxide build-up on the probe. The latter gives rise to time lags in both the temperature measurement and the control loop response — a typical outcome is temperature cycling.

With the Heubach ball-mill plants, the lead feed is in the form of solid lead cylinders of ~100 g in weight. The dosing rate is adjusted so as to maintain a constant hold-up in the mill. The distribution within the mill is critical and a patented device has been developed to achieve optimum conditions. The process temperature is measured by the air flow leaving the mill and is controlled by the injection of water. The system exhibits very good temperature control (i.e., ± 3 °C) and produces no waste water. Again, the key feature is the relatively fast response time for this loop, as compared with a water spray on the outer surface of the mill.

Both the Barton-pot and ball-mill plants are equipped with modern programmable controller units that allow a high degree of monitoring and the installation of alarm functions. The latter units also have the facility for connection to a supervisory computer for data collection as part of a quality monitoring system.

A recent modification has resulted in the development of a new, high-quality, Barton oxide. The characteristics of this new oxide are compared with those of a standard Barton-pot oxide in Table 2. It can be seen that the main features of the new oxide are: (i) a significant reduction in the fraction of particles >63 μm, i.e., far fewer larger particles; (ii) a higher surface area and acid absorption, this implies a generally finer product. In addition, the new modification allows the Barton reactor to be run more safely at lower temperatures. The advantage of lower temperature operation is that a higher fraction of the oxide is produced as α-PbO which brings advantages in the paste-making processes. One final advantage is that dross oxide (~1 to 2% of lead through-put) can be recycled in this new system.

Costs

Developments regarding costs have focused particularly on investment or capital costs for new plants. With the high degree of automation, the operating costs of

TABLE 2

Comparison between normal Barton-pot oxide and the new oxide

	Standard oxide	New oxide
Specific surface area (BET) ($m^2 g^{-1}$)	<1	c. 1
Scott density (g ml^{-1})	1.3–1.6	1.3–1.4
Tamped density (g ml^{-1})	3.5–4.0	3.3–3.5
Sieve residue, 63 μm (%)	0.2–2	<0.1
Acid absorption, H_2SO_4 (mg/g oxide)	140–180	200–230

Heubach oxide plants can be tightly controlled. The personnel requirements for the ball-mill plant are only associated with the loading of lead ingots onto the ingot conveyor for the melting kettle. With the Barton-pot plants, it is estimated that one worker can operate five reactors.

In the battery oxide field, the most recent development of interest is a very compact unit for the production of red lead. The design of the unit is based on a stirred reactor principle and operates in a semi-batch mode. Normal highly-oxidized monoxide is fed to the reactor along with a supply of pure oxygen. Once a batch is completed, the contents are discharged and a fresh batch of raw monoxide is charged. The cycle time of this process is 20 min; this is appreciably less than the normal cycle time of many hours. Such units operate fully automatically with a throughput of ~3 to 12 t/day, and when compared with the equivalent traditional oven are far smaller and have a lower capital cost.

Outside of the battery field, a similar stirred reactor has been developed for the production of high quality litharge (99.99% PbO) in a one-step process. The reactor operates in two distinct stages: a lead feeding oxidation stage followed by a short final oxidation stage. Again the cycle time is around 20 min. Operation of the unit is totally automatic and the unit has a significantly lower capital cost per tonne than the equivalent standard litharge plant.

The development of these small, low capital cost units enables red lead and litharge production to be considered by smaller producers.

Environmental performance

There are three main areas to be considered: (i) dust emissions; (ii) energy utilization; (iii) workplace noise levels.

Lead emission, in any form, is a sensitive issue both in the workplace and in stack emissions. The Heubach plants are all fitted with filters on the exhaust gas exit. These are specially developed for lead oxide duty and enable exhaust emission levels of <0.1 mg Nm^{-3} to be guaranteed.

Regarding the oxide levels in the workplace, all the Heubach plants are operated under suction and all melter units are fitted with a suction hood. The oxide level in the workplace depends very much upon the prompt clearing up of any oxide. For this purpose, the installation of a well-designed vacuum system is strongly recommended.

The main heat sources in both the Barton-pot and ball-mill plants are the lead-melting device and the reactor and mill units. One important area where improvements in energy utilization are being made is in the melting unit. With gas heating, a heat recovery unit is offered. With both the gas and electric heating, an improved heat

insulation is being developed to reduce losses. To retrieve useful energy from the plant exhaust gas, a heat recovery system is offered and can be used for space heating.

Finally, major sources of workplace noise with both the Barton-pot and ball-mill units are the filter plant and exhauster fan. In Heubach plants, the fan is mounted on vibration reducers and the main unit is lagged with sound-proof cladding. Levels of ~80 dBA are achieved and can be reduced if required. The mill unit itself is a particular noise source and must be enclosed in a sound-proof housing.

In summarizing, the aim of this work is to supply plants that produce high-quality oxide that is tailored to the customers' requirements and has a high degree of automation and environmental performance.