BRITISH MINING No.73

MEMOIRS 2003

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Gray, G. & Judd, A.G., 2003
"Barium Sulphate Production
from Mine Waters in
South East, Northumberland"
British Mining No.73, NMRS, pp.72-88

Published by

THE NORTHERN MINE RESEARCH SOCIETY
KEIGHLEY U.K.

ISSN 0309-2199

BARIUM SULPHATE PRODUCTION FROM MINE WATERS IN SOUTH EAST NORTHUMBERLAND

G. Gray and A.G. Judd

Abstract
Barium-rich brines encountered in the Beaumont seam at the Eccles Colliery, Backworth, were exploited for the production of barium sulphate ('blanc fixe') between 1937 and 1969. The $BaSO_4$ was precipitated when the brines were mixed with sulphuric acid, drawn off in filter presses and sold commercially. Additional barium brines were produced by the reaction of hydrochloric acid, a by-product of the precipitation process, with witherite (naturally occurring $BaCO_3$). These were then introduced into the precipitating process, as were additional brines piped from the Rising Sun Colliery at Wallsend.

The quality (particle size) of the product could be varied by careful adjustment of four parameters: the temperature, the strength of the sulphuric acid, the rate of flow of the brines, and the introduction of the acid into the decanters (the precipitating vessels). The precipitated barium sulphate was drawn off as a pulp into filter presses then emptied into polythene-lined casks or oven dried. It was then milled and bagged ready for sale. The effluent was neutralised with dolomite and suspended solids were allowed to settle before discharge into a local stream.

These collieries were not the only collieries in the North East coalfield to encounter barium-rich minewaters. However, their brines were the strongest, and most prolific.

Keywords: Barium, Blanc Fixe, Minewaters, North East Coalfield

Introduction

Mine Waters have always caused problems in the mining industry, but particular problems encountered in south east Northumberland came in the form of waters containing barium chloride. This is extremely poisonous, and, when combined with waters containing sulphates, produced dense milky deposits. The concentration of the barium brines generally varied from very weak to several hundred parts per million; they also contained significant amounts of sodium chloride and small quantities of magnesium chloride. These waters could be managed by having mixing and settling ponds underground near the shaft bottom. These ponds could be cleaned out regularly and the crude precipitate put onto spoil heaps. However this solution worked only when the waters occurred in relatively small quantities.

History

In 1929 an unusual water was broached in the South Dip district of the Beaumont seam in the Eccles Colliery, Backworth (see Figure 1 for location).

This water, which occurred in considerable quantity, was clear of suspended matter, had no inherent iron, and contained 4000 ppm (mg.1^{-1}) of barium chloride. (A previously published analysis of these waters is presented as Table 1).[1] It caused immediate problems.

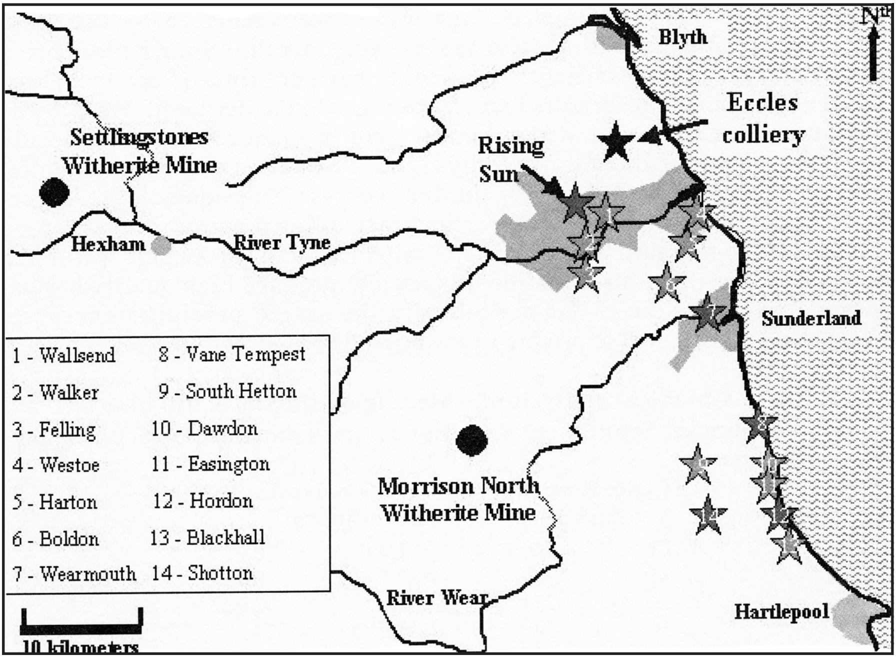

Figure 1. Location map.

The volume could not be dealt with in the usual manner; the amount of barium chloride present in solution could not be precipitated out without causing large amounts of crude barium sulphate to be produced, and this amount could not be placed with the normal colliery spoil. For a few years the barium sulphate was stored in the old workings, and the waters were pumped to the Surface and into the Briar Dene burn to disgorge into the North Sea about 5km away. Due to the crude treatment of the brines, sometimes the dissolved barium chloride had not been fully precipitated. This meant that the discharged waters were poisonous; a hazard to humans and particularly to animals who drank from the stream.

From 1929, experimental work was carried out in the colliery laboratory into the various ways to treat the barium brines, to minimise the pollution and, if Possible, to produce a saleable product. As a result of this research it was decided to build a 'Water Treatment Plant'. This was accomplished in 1937. Research continued throughout the 33 year production life of the water treatment plant (known as the 'Barium Plant'). During this time many of the improvements to the production process resulted from daily observations, and trial and error. Because this was the only such plant operating using natural barium brines, no reference data were available.

Initially, sulphate-rich waters from the High Main seam in the nearby Maude Colliery were used as the precipitating agent, but this did not prove successful. In 1939 the sulphate-rich waters were replaced by sulphuric acid. Then an attempt was made to qualitatively mix the strong barium brine (from the Beaumont seam) with the weaker barium brines (from the Three Quarter Main) in the reservoirs before leading it to the decanter. Here it was precipitated with concentrated sulphuric acid introduced through a needle valve, the quantity being measured by sight. This failed at the first attempt, and a second attempt attained very limited success. Subsequently the waters were kept separate in the reservoirs and drawn off as required, and a method was devised to measure the quantity of sulphuric acid used. This was much more successful. The strong brine was used to produce high quality barium sulphate ('Blanc Fixe'), but periodically the single precipitating vessel (decanter) was switched to produce a lower grade product from weaker brines.

Table 1: Chemical analysis of waters from the south dip district, Beaumont Seam, Eccles Colliery (after Edmunds, 1975[1]).

	Concentration ($mg.1^{-1}$)		Concentration ($mg.1^{-1}$)
Ca	4,600	Cu	0.02
Mg	700	Ni	0.05
Sr	273	Zn	0.022
Ba	340	HCO_3	124
Na	18,250	$S0_4$	<1.0
K	225	Cl	38,980
Li	8.8	F	0.21
Rb	0.60	Br	360
Fe	0.4	I	1.4
Mn	4.4	H_3BO_3	1.8
Cd	0.0015	Co	0.028
Total	**63,870**		

Before World War Two a considerable amount of barium sulphate was imported from Germany, but with the outbreak of war, of course, this stopped. The War Department immediately made a priority order for barium sulphate produced at Backworth for use in the manufacture of photographic prints, principally for the Air Ministry. The remaining production was taken up by other barium sulphate users, and there was insufficient to satisfy the demand.

A second decanter was built making production much easier: No.1 decanter could be used solely for the strong brine, whilst No.2 was used for the weak brines. Subsequently the process was extended to utilise the effluent from the manufacturing process, mainly hydrochloric acid. Barium carbonate, in the form of the mineral witherite, was processed using the hydrochloric acid to produce additional barium chloride. A third decanter was built for the weak brines, and decanter No.2 was released for processing the stronger brines. The output from the plant then rose from 661 tons (672 tonnes) in 1939 to over 3,000 tons (3048 tonnes) per year at maximum production.

With production at the plant running twenty four hours per day, seven days per week throughout the year, and with other producers of barium sulphate in the country, most war time demands could be met. However, after the war it did not take Germany very long to once again produce barium sulphate so, competition between producers started once more. The quality of the product, and manufacturing to customers specifications became very important.

In 1961 in the Rising Sun colliery at Wallsend, 6.5 km from Backworth, the Three Quarter Main seam was producing a weak barium brine containing a considerable amount of iron (in solution and in suspension). These waters were causing pumping troubles, blocking the rising main with precipitates and polluting a stream and a lake. To relieve this problem a double pipeline was laid to Backworth and 300,000 gallons (1,363,800 litres) per day were pumped for processing at the Barium Plant, enabling the Rising Sun to remain open. To keep the pipelines open they were cleaned out regularly by passing through them a ‘pig’ scraper device. The ‘pig’ contained a radioactive source to locate it, if it became stuck.

Between 1937 and 1970 various grades of barium sulphate were produced to customer specifications; details of the products and their uses are presented in Table 2.

Table 2: Barium sulphate products

Grade	**Average particle size microns)**	**Pulp or Dry**	**Minimum $BaSO_4$ content (% dry basis)**	**Uses**	**Special Properties**
Photographic and X-ray	1.5	P	95	Bromide paper Barium Meal	Free of: S, Fe, As, poisonous metals
Standard	2.0	P	93	Paper coating (glossy)	Free of oversize & foreign matter
Matt	8.0	P	90	Paper coating (matt)	Particle size
Standard	2.0	D	95	Paint extender, filler, inks	B.S. Specification
Semi-transparent	3 – 4	D	93	Rubber filler, paints	To customers’ requirements
Transparent	5.0	D	91	Pigments and colours. asbestos filler	Particle size

The following account, which describes the process used at the Barium Plant may be useful, if in the future, the strong barium brine which is still underground and readily available with modern mining methods, is used for manufacture of barium sulphate.

Raw Materials

The fundamental production process, summarised in Figure 2, depended upon the following chemical reactions:

$$BaCl_2 \text{ (brines)} + H_2SO_4 \longrightarrow BaSO_4 \text{(Blanc Fixe)} + 2HCl$$

$$BaCO_3 \text{ (witherite)} + 2HCl \longrightarrow BaCl_2 + H_2O + CO_2$$

From this it can be seen that three raw materials were used: the chloride-bearing brines, sulphuric acid and witherite.

Brines

In the Eccles colliery, the strong barium brine in the South Dip district was by-passed by the coal workings. So, a dam was created and a pipeline laid to the shaft bottom. Here a standage was prepared. With the gradient in this district it was possible to siphon the brine to this standage, thus there was very little disturbance to the brine and it was not contaminated by the coal workings. The weak barium brines in the Three Quarter Main seam were pumped from the various points in the seam to a separate standage at the shaft bottom. From here the brine was pumped to the surface at times specified to suit the production plant. About 180,000 gallons (818,280 litres) of brine per day were processed.

From the Maude Colliery a water in the High Main Seam containing soluble sulphates was pumped to a separate standage at the shaft bottom then to the surface reservoir as required.

There was one reservoir for the strong brine, three reservoirs for the weak brines (because of their greater volume and contamination), and one reservoir for the sulphate water. The reservoirs were about fifteen feet (4.6 m) deep and as the waters were pumped into them from underground they each passed through a large pipe drilled with graduated holes, small at the inlet and becoming larger towards the end. This pipe was suspended so that there was a drop of about three feet (0.9 m) to the surface of the reservoir. This drop aerated the water and so bringing into suspension the inherent iron. The size of the reservoirs was such that there was time for these suspended solids to settle to the bottom of the reservoir. The accumulated sludge was cleaned out at regular intervals.

Two large reservoirs, each holding about 500,000 gallons (2,273,000 litres), were created to hold the waters from the Rising Sun colliery. These waters were very much more ferruginous than the Backworth waters. They were also slightly acidic. In addition to oxidation by introducing air, a measured solution of sodium hypochloride was introduced. This caused the dissolved iron to flocculate and settle.

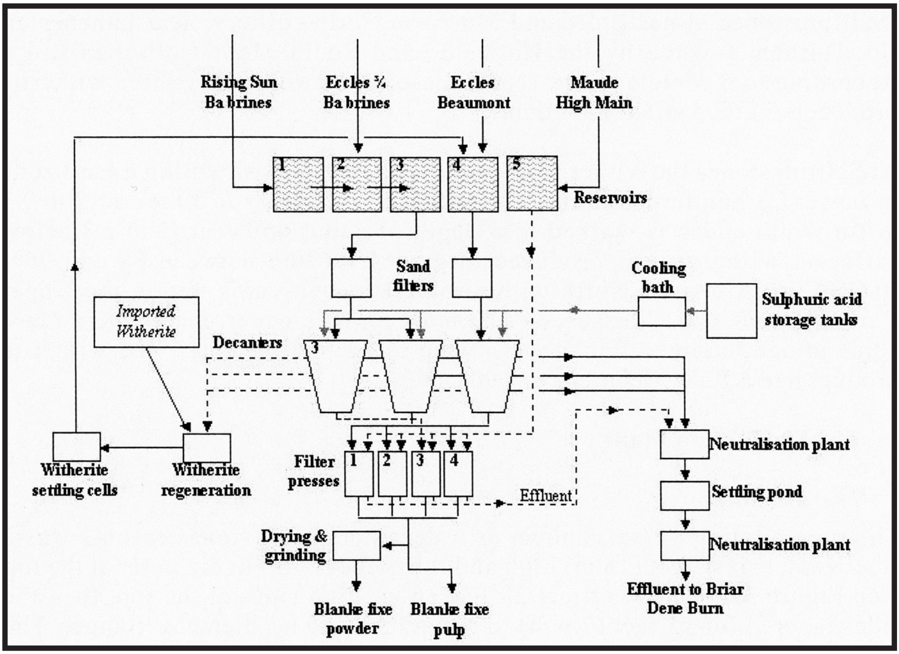

Figure 2. The barium sulphate production process.

All the pipelines carrying barium brines into the plant were lined with hard rubber and, wherever possible, nickel/cast iron bends and fittings were used. The barium brines were drawn off from the reservoirs with centrifugal pumps which had phosphor-bronze impellers to protect them against corrosion. The brines were passed through gravel and sand pressure filters before they entered the decanters.

Sulphuric Acid

Industrial quality concentrated sulphuric acid was used. In the early stages this acid was stored in two lead-lined tanks. The acid was found to contain significant amounts of suspended solids from the manufacturing process. Attempts were made to filter the acid using sintered filters such as Doulton Candles, but the amount of suspended solids was so great this was not practical. The final solution was to have more, larger tanks to allow the Solids to settle out; this proved quite successful.

The acid was pumped from the tanks with 'Tungstone' lead pumps (over the years these pumps were very successful) to the top of the decanter into a head tank.

Witherite

Witherite, natural barium carbonate ($BaCO_3$), was acquired from two local sources: Settlingstones mine, near Fourstones, Northumberland (Settlingstones Mines Ltd.), and Morrison North colliery, near Lanchester, Co. Durham (owned by the Holmside and South Moor Collieries Ltd.). According to a contemporary report these were two of only three Witherite producers in the United Kingdom.[2]

At Settlingstones the Witherite occurred as a vein deposit within a fault zone in Lower Carboniferous strata. The witherite lode was 4 to 30 feet (1.2 to 9.1 m) in width and was worked to a depth of about 650 feet (200 m) below surface. Witherite was produced in grades varying between 88 and 96% $BaCO_3$. At Morrison North Witherite occurred in veins within the Upper Carboniferous Coal Measures. The most prolific occurrence, where these veins joined, attained thicknesses of up to 22 feet (6.7 m). The Witherite product had a $BaCO_3$ content of >90%.[3,4,5]

The Production Plant

The Decanter

The precipitating vessel, known as a decanter for obvious reasons, was a steel vessel sixty feet (18 m) high and thirty feet (9 m) in diameter at the top (see Figure 3). It had vertical 20 feet (6 m) high sides at the top, then the sides tapered for 25 feet (7.6 m) to a two feet (0.6 m) diameter flange. The flange was a seal containing two six inch (15 cm) diameter flanged pipe junctions from which to draw off the contents. The decanter was lined with rubber, as were all the pipes and fittings which had contact with the contents.

In the centre of the decanter, supported from the top on cross girders, was an eight feet (2.4 m) diameter tube ten feet (3.0 m) long known as the 'curtain' (the purpose of which is explained below).

Introducing the brine

The main brine distribution point, known as the 'basket', was at the top of the curtain (see Figure 4). This was a trough, in the shape of an annulus six feet (1.8 m) in diameter. The trough was one foot (30 cm) square in section, giving a central hole four feet (1.2 m) in diameter. The brine was introduced into the base of the trough at one point, from which it circulated in both directions. Inside the trough there were baffles to even the flow of water. The trough was capped by 3/4 inch (19 mm) conveyor belt rubber. This rubber had 1 inch by 3/8 inch (25.4 and 9.5 mm) slots, arranged in concentric rings, through which the brine rose evenly to flow towards the centre of the annulus.

At the centre, on top of the rubber, was a 'control ring'. This steel ring had a central hole whose inner edges were shaped to a prepared curved template. The brine flowed through the control ring, and down into the decanter where it formed a vortex. The size of control ring installed determined the diameter of the vortex.

The basket was suspended from a raised section on the top of the decanter by four stainless steel threaded rods. By adjusting these rods the basket was kept level (ensuring an even flow of water into the decanter) and the bottom of the basket was held one foot (30 cm) above the highest level of the solution in the decanter.

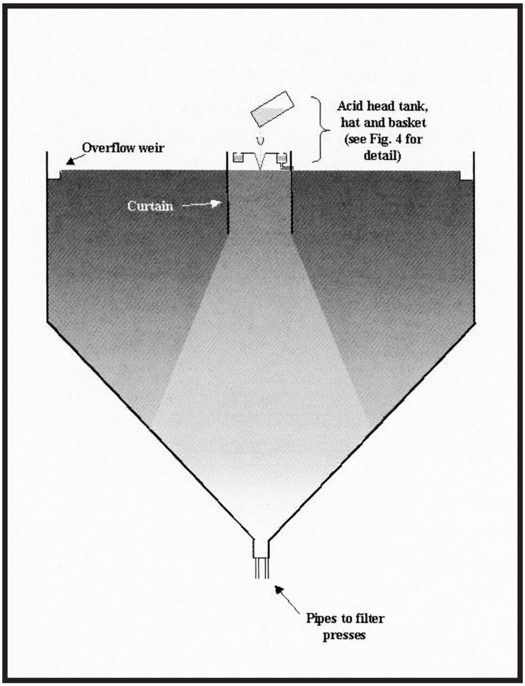

Figure 3. The precipitating decanters

Introducing the sulphuric acid

The sulphuric acid head tank, which was five feet (1.5 m) long and two feet (0.6 m) in diameter, was suspended at an angle of approximately forty five degrees (this angle was adjustable) with an acid inlet at the upper end (also shown in Figure 4). On the lower side there were eight 1.0 inch (2.5 cm) flanged outlets. The top outlet, which was open, was an overflow which fed back to the tanks through a sight glass in the control room; this enabled a constant overflow to be readily observed. The remaining seven outlets had valves. The lowest outlet was a drain valve so that the head tank could be washed as required. The other six outlets, spaced at equal distances, could be opened or closed as required. Initially the highest one would be opened, making this the overflow. During production the aim would be to run on the centre valve, thereby allowing movement up to increase, or down to reduce the flow of acid, depending upon the ambient temperature fluctuation. Additional, finer, control of the flow rate could be achieved by varying the angle of the head tank.

Between the lowest adjusting outlet and the drain valve was a tee piece from which ran the acid required for the precipitation. This acid could still contain some suspended matter so a filter device was used (see Figure 5). This consisted of an arrangement of four ¼ inch (6 4 mm) thick lead discs separated by sheets of pure rubber. As the acid entered this device the first lead disc it encountered was perforated with a circular pattern of holes drilled with an accurate twist drill. The second and third lead discs had similar patterns of holes, but of successively smaller diameter. The final (fourth) 'control' disc had a single central hole whose diameter was between that of the holes in the previous two discs. This arrangement proved to be very effective for the filtration of the suspended solids provided the discs were cleaned at regular intervals.

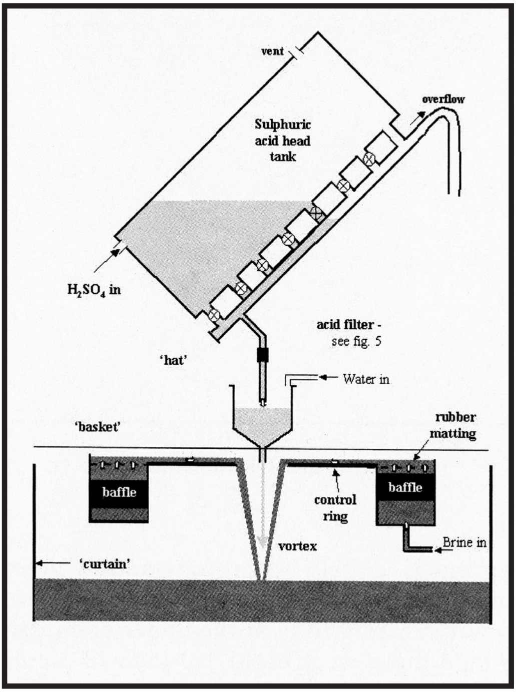

Figure 4. The basket' – introducing the brine and the sulphuric acid to the decanter.

From the control disc the acid was run into a small lead mixing vessel (the 'hat'), one foot high by one foot (30 cm x 30 cm) in diameter. Here tap water could be added as required through a similar control disc. A refrigeration plant was installed so that in summer the acid could be cooled. Steam heating of the acid was attempted for the winter but this was found to be dangerous and not particularly effective; introducing tap water as a dilutant proved effective and very much simpler. Acid of the required temperature and strength was run into the decanter through a lead tube. This tube was flexible enough to be adjusted so that the acid flow could be directed into the centre of the brine vortex about a foot (30 cm) below.

All the pipes and fittings of the acid system were lead lined, and the pipes were of regular lengths of four, six and eight feet (1.2, 1.8 and 2.4 m) so that spares could be kept to replace leaks due to wear and tear.

Barium Precipitation

The mixing of the brine and sulphuric acid in the vortex caused barium sulphate to precipitate. The precipitate was directed towards the bottom of the decanter by the curtain which stopped it spreading sideways. The time taken for the precipitate to settle depended upon the particle size. Precipitates with large particle sizes settled readily, but when the process was set up for a high grade product these smaller particle sizes settled much more slowly.

The settling time also determined the through-put of the brine. The effluent overflow into weir at the top of the decanter maintained a constant level at the point of precipitation.

Blanc Fixe preparation

The barium sulphate pulp was then drawn off by gravity feed into filter presses. There were two large filter presses each holding one tonne of pulp, and two smaller presses each holding half a tonne. When each press was full, the valves to the witherite vessels and the decanter were closed. Sulphate-bearing water from the High Main Seam was taken from the reservoir, through a sand/gravel filter and used to wash the pulp free from acid.

When the filter press was ready to be emptied it was opened revealing, in each frame, a filtercake about one inch (2.5 cm) thick with a moisture content of about 25%. A wooden knife was run around the outside edge, then down the centre, and with a man at each side, the cake was rolled down and placed into a polythene-lined cask, or when required, into an aluminium drying tray. The material in trays was oven dried then milled, bagged and sampled.

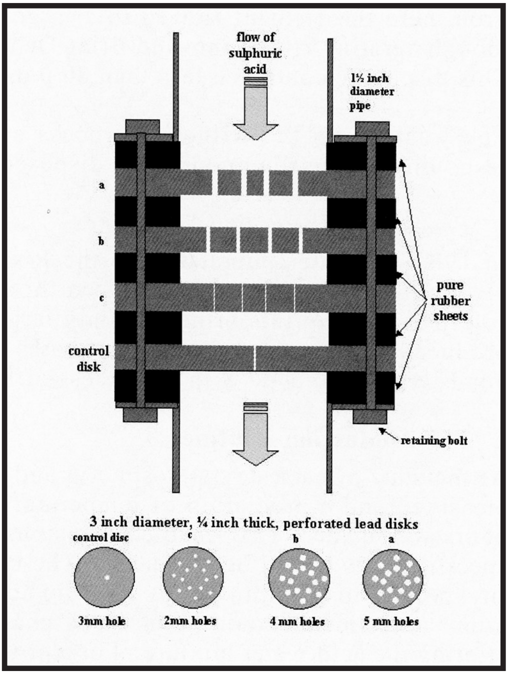

Figure 5. The sulphuric acid filtration equipment.

When X-ray quality barium sulphate was being made the pulp was given a final wash with tap water to clear any harmful contamination. When necessary, compressed air could be introduced into the filter press to blow out any excess water, but this was usually only required when large particle sizes were being produced.

Witherite processing

The hydrochloride-rich effluent from the decanters was mixed with witherite in rubber-lined tanks. The resulting 'regenerated brine' was then passed through a pipeline to one of the brine storage reservoirs where it was mixed with the brines (normally those from the Beaumont Seam).

Effluent management

The effluent from the decanters not required for witherite regeneration was piped to treatment ponds. Also, waste water from the filter presses ran into a rubber lined trough under the filter press and then through pipes into the treatment pond. [In order to monitor the reduction in chloride content at the filter presses, periodically a sample of the waste water was taken for testing with a weak solution of silver nitrate solution.] This treatment pond, located outside the plant, was quite large and contained several tonnes of dolomite, (Mg, Ca)CO_3. The dolomite neutralised any remaining acidity in the effluent. From here the effluent flowed to a large settling pond which overflowed though aerating riffles into the Briar Dene burn, discharging it to the sea. This discharge contained less than 80 p.p.m. suspended matter.

The waste from the witherite process and the sludge cleaned from the reservoirs and settling ponds was disposed of with colliery waste.

Processing the Rising Sun brines

In 1961 the water pumped from the Rising Sun colliery created special difficulties in processing at Backworth; the No.3 decanter was devoted solely to treating this brine and only large particle size material could be produced. The limestone treatment baths were enlarged and more settling ponds created to cope with the excess effluent.

The Production Routine

At the start of each day atmospheric and barium water temperatures were measured and a prediction of temperatures for the following twenty four hours was made. This enabled decisions to be made on which customer specifications would be produced. The control ring in the basket was the first control to be put in place. This did not have to be changed each time as minor adjustments could be made by changing the volume of the brine or altering the acid/water mixture. For a product with a small particle size the vortex in the centre of the ring was usually half to one inch (1.3 to 2.5 cm) in diameter; increases in this diameter to a maximum of about six or seven inches (15 to 18 cm) resulted in the precipitation of larger particles.

The acid control disc was then put in place and the acid was either cooled or diluted with tap water, as necessary. The barium brine was then pumped through the sand/gravel filters up to the decanter top, and as it overflowed the control ring the acid was introduced through a flexible lead tube, directly into the centre of the vortex. If necessary this was accomplished by moving the flexible lead tube.

Quality Control

The operating parameters were such that when precipitating out the barium chloride the resulting effluent had to be as near the full precipitation point as possible. If too much acid was used calcium sulphate was also precipitated.

contaminating the barium sulphate. Excess acid polluted the stream. Insufficient acid left residual barium chloride in the effluent. These parameters were monitored by regular sampling and laboratory testing (see following section).

Delicate control of the precipitation process ensured that the barium sulphate was manufactured to customers' specifications. The following parameters were critical:

1. Temperature

Two degrees centigrade difference in the water temperature and ten degrees difference in the ambient temperature made it necessary to make adjustments to the process. To this end temperature recorders were installed and monitored at regular intervals. The acid could be cooled in a refrigeration process. However, if the acid was too cold heating was not practical. In this case dilution was necessary.

2. Strength of the sulphuric acid

This could be varied by introducing measured amounts of tap water.

3. Sulphuric acid flow rate

The flow rate could be varied by two methods. A coarse control was achieved by selecting, for the filtering apparatus, control discs with an appropriate range of holes sizes. In particular the diameter of the single hole in the final lead ('control') disc determined the flow rate. However, a finer control could be achieved by adjusting the valves of the head tank. The selection of a particular valve determined the head of acid in the tank, and therefore the pressure and the flow rate at the outlet.

4. Brine introduction - pressure control

The barium brine was pumped up to the decanter through a fine threaded gate valve. The volume could be regulated by adjusting the pressure to between 30 and 40 p.s.i. (207 to 276 kpa).

5. Brine introduction - vortex control

The most important control was found to be the actual method of introducing the barium brine into the decanter. This could be used to make a great difference in the particle size of the barium sulphate produced. To do this control rings of various sizes, internal diameters of 10 to 18 inches (25 to 46 cm), were available. One of these would be selected and placed on the slotted rubber in the basket. The brine would then drop into the decanter in an even vortex with a central hole measuring from one foot to half an inch (30 to 1 cm), depending upon which control ring had been selected.

6. Brine : acid mixing

Finally, it was critical that the stream of acid could then be introduced in the very centre of the brine vortex. This was achieved by adjustments (made by hand) of the flexible lead tube at the base of the hat.

Together, these adjustments provided absolute control of the particle size of the product. However, it was only through the experience of years of trial and error that the importance of these controls was realised, and methods of achieving them were developed.

Simple laboratory tests were devised to enable any required adjustments to be identified. An effluent sample was taken hourly and tested against tenth-normal sodium carbonate solution to measure the excess acidity. Two test tubes were part-filled with the filtered effluent. A weak solution of sulphuric acid was added to one, and a weak solution of barium chloride to the other. After being shaken, the test tubes were allowed to stand for a few minutes. For full precipitation to have occurred a slight precipitation should have been visible in each tube; if this was not the case adjustments could be made to compensate. Various turbidity meters were tried but it was found that there was no substitute for experienced sight testing.

Product Testing

A sample of the pulp was taken for analysis before any of the production left the plant. A range of tests were conducted to ensure that the product met customer specifications.

1. Moisture content

Moisture content was measured by the standard method: a sample was weighed, heated to 100°C to drive off water, and then re-weighed. Moisture contents were calculated as a percentage of the original mass.

2. Particle size

Particle size analyses were undertaken using the following settling test method: 50 gm (dry basis) ofthe pulp was mixed with distilled water to a thin paste; this was done carefully so as to avoid breaking up the particles. This sample was then washed into a stoppered 500ml measuring cylinder, made up to 500ml with distilled water, and shaken for 5 minutes. The supernatant liquid was measured at intervals of 5, 15 and 30 minutes, and then again after 24 hours. The five minute reading gave an indication of the particle size being produced, and the other three test results indicated whether or not there had been any mixing of particle sizes during the change over from one product grade to another. A certain amount of contamination was inevitable during changes between customers' specifications, but affected material could be carefully mixed with the coarser (five micron size) product and used in asbestos fillers.

The settling test results were validated by correlation with particle size analysis results from an independent laboratory. The method was found to give a very good indication of the particle size of the product.

3. Colour (whiteness)

A pure white colour is essential for barium sulphate. Every batch produced was checked against colour reference samples maintained in the laboratory. An artificial north light box was used in the comparison, but, once again after testing various meters, experienced sight testing was found to be the most reliable.

4. Purity

Part of the X—ray quality sample was sent to an independent analyst to certify that it was of sufficient purity for human consumption.

Disposal of Plant Effluents

Before 1936 the mine waters were disposed of with little thought of pollution or the effects on the local population. Water from the standages at the shaft bottom were pumped to the surface where it was stored in a pond. Water not required for the production of steam to run the winding engines (for hauling the cages up the shaft) ran into a stream which flowed eastwards past the village of West Holywell through arable land, and then into a reed bed. After 1929, when the barium-rich brine was encountered, the waters in the reed bed were contaminated, and some grazing animals drinking from it were killed. The stream continued eastwards as the Briar Dene Burn, eventually discharging into the sea through the Links (between Whitley Bay and St. Mary's Island).

When the Barium Plant was first opened very little was done to improve this situation. However, when sulphuric acid was introduced to the process the pollution problem was taken seriously. All discharges of waters from the mine and the Barium Plant were monitored throughout each day, seven days per week. The underground pipelines and standages were checked weekly to avoid contamination between the waters.

Initially the effluent discharge from the Barium Plant was kept acidic so that, once mixed in the stream with the mine waters, there was a slight acidity. This was not enough to affect the wildlife or grazing animals, but it did keep in solution the considerable amount of iron in the discharges. In turn, this kept the burn looking presentable. With rectangular weirs and vee notch measuring equipment on the mines discharge and the plant effluent, the flow could be reasonably well controlled during times of heavy rainfall and flood. Control was effected by varying pumping times and the regeneration of effluent into barium chloride or discharge as necessary.

When the National Rivers Authority (NRA) was formed the Barium Plant was categorised as a factory, so strict effluent water control measures were required. The NRA decided that the burn should be kept alkaline rather than slightly acid. The consequence of this was that the suspended iron precipitated, turning the burn water brown and causing the deposition of the brown precipitate on the stream bed and sides. This evident pollution was not popular, so aeration plants and settling ponds were introduced. During this period, because the colliery was not a factory, the minewater flow the from the pit head, which mixed with the outflow from the Barium Plant, was not subject to the same pollution control legislation. When coal was being cut in seams with a considerable water flow, the minewater outflow was so black with suspended small coal particles no other pollutants were visible. Nevertheless the NRA did not concern themselves with this.

Mine Closure

The Rising Sun Colliery was closed in 1969 and the Three Quarter Main brine was allowed to flood the mine. In 1970 it was decided to close the Eccles Colliery with automatic closure of the Barium Plant. After further deliberations by management, it was decided to reprieve the Eccles Colliery. The Barium Plant had always been in profit and contributed to the pumping costs of the colliery, but with the wisdom of higher management, it was decided that the plant would close. From the closure of the Barium Plant in December 1970 until the closure of the colliery some years later, the barium waters from the Eccles Colliery were precipitated in the surface reservoirs and a worthless product was dumped on colliery spoil heaps. Full circle had been achieved.

The Eccles Barium Brines in Context

When the coal mining industry was nationalised in 1947 a survey of all the minewaters in the northern coalfields (Northumberland, Durham and Cumberland) was undertaken (by the first author) to see if there were any other barium brines of sufficient strength for the manufacture of barium sulphate. In the course of this survey, which took almost two years to complete, every mine in the coalfield was visited, and in each mine all sources of minewaters were tested for barium and sulphate content. In addition the acidity and temperature were measured. Any waters testing positive were sampled, and more rigorous analyses were undertaken at the Backworth Barium Plant. The results of this survey showed that there were no other minewaters with a barium content as high as that from the Beaumont Seam in the Eccles colliery. However, some waters did have sufficient barium, and great enough volumes of water to make economic barium sulphate production possible. In each of these cases flow measuring equipment was set up. Flow rates were measured and samples were taken (in large carboys) at 15 minute intervals for 14 days. The samples were analysed for: suspended solids, dissolved solids, pH, dissolved iron, barium as sulphate, calcium as sulphate, and magnesium as sulphate.

A few sources, particularly some in County Durham, were considered economically viable, but funds were not found to develop them. The results of the survey were not published.

Subsequently, Edmunds (1975) reported on a study of the geochemistry of brines in the North East coalfield. He reported that 100 representative analyses of brines from working mines were "extracted from the records of the National Coal Board" (possibly a report of the above-mentioned survey), and new analyses of samples from selected locations were undertaken.[1] Edmunds reported significant (i.e. >1,000mg.L^{-1}) concentrations in waters from Wearmouth, South Hetton, Vane Tempest and Horden collieries (all in County Durham), but none were as concentrated as the waters from the Eccles and Rising Sun collieries. Smith (1981) also noted the existence of barium in some minewaters in north-east England.[6] Apart from the Eccles colliery, he reported that a "relatively weak brine" was being pumped from Boldon colliery, and he identified the following collieries as having recorded barium brines (although no details were offered): Eccles, Rising Sun and Wallsend north of the River Tyne; Westoe, Walker, Wearmouth, Harton, Boldon, Felling, Vane Tempest, South Hetton, Shotton, Dawdon, Easington, Hordon and Blackhall south of the River Tyne. [The collieries mentioned here are shown in Figure 1.]

Conclusions

Over a period of 33 years the Barium Plant at the Eccles Colliery, Backworth, pioneered the commercial production of barium sulphate ('blanc fixe') from barium-rich minewaters. The method of precipitating the barium sulphate was developed and perfected, enhanced by the introduction of witherite ($BaCO_3$) from other mines, and extended to cater for barium brines from the Rising Sun colliery, Wallsend.

Although these minewaters were unusually rich in barium, other barium brines were identified in the North East coalfield. However, no other minewaters were exploited.

The Barium Plant was closed when it was still profitable, and since the closure of the colliery this resource has remained underground.

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Paper received 6 October, 2003

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