PROVINCE OF ALBERTA

Research Council of Alberta — Report No. 53

University of Alberta, Edmonton, Alberta.

The Role of Very Fine Mineral Matter in the Hot Water Separation Process as Applied to Athabaska Bituminous Sand

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EDMONTON
PRINTED BY A. SHNITKA, KING'S PRINTER
MARCH, 1949

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THE ROLE OF VERY FINE MINERAL MATTER IN THE HOT WATER SEPARATION PROCESS AS APPLIED TO ATHABASKA BITUMINOUS SAND

Abstract

The clay present in bituminous sand as a natural constituent plays a key role in the hot water separation process. Some clay is necessary for satisfactory results; more than enough decreases the yield of oil. When bituminous sand is mixed and heated with water into a mortar-like pulp preparatory to separation, the clay present causes the oil to disperse into flecks lying unattached among the sand grains. These oil flecks vary in size and in the amount of clay associated with them. On flooding the pulp with hot water the oil flecks of low clay content float on the surface as froth. The flecks of higher clay content become dispersed in the water. Increase of clay in the bituminous sand causes increase in the proportion of oil which disperses. When bituminous sand is removed from the deposit and is stored, a change of association between oil and clay which is detrimental to the hot water separation process tends to take place.

INTRODUCTION

The recovery of oil from the Athabaska bituminous sands has been under study by the Research Council for years. The early work consisted in making many laboratory runs on bituminous sands from different locations under varying experimental conditions in the hope of uncovering the factors which were operative in the hot water separation process. Considerable progress was made. The point was reached where it was considered possible to formulate a number of theoretical statements about the bituminous sands themselves and about the way this aggregate reacted when treated with hot water in a separation operation (2). These statements were:

(1) Bituminous sand is an aggregate of sand, clay, oil and water. The sand consists mainly of quartz particles of 100 to 200 mesh size and smaller, but also of particles of other minerals including mica, rutile, ilmenite, tourmaline, zircon, spinel, garnet, pyrite and lignite. Clay occurs interbedded with the bituminous sand of which, also, it is a constituent. Ironstone nodules of all sizes up to eight inches in diameter are likely to be present in the bituminous sand beds. The oil is viscous, naphthenic and of a specific gravity slightly greater than that of water. The oil content ranges up to, and sometimes even exceeds, 17% by weight. Rich bituminous sands from beds not

invaded by water have a water content of 3 to 5% by weight. The water is probably present as a film around the sand particles. The oil surrounds the moist sand grains as an envelope.

(2) Water wets quartz and other siliceous minerals more readily than does mineral oil. Consequently water tends to displace the oil films surrounding the quartz and other siliceous particles when the bituminous sand is mixed with water. Whether the oil is completely displaced depends on the properties of the water. That is to say, the materials dissolved or suspended in the water modify its wetting properties.

(3) When bituminous sand is mixed with water, substances present dissolve or become suspended in the water and determine its ability to displace the oil from the sand surfaces. This ability is a function of the concentration of substances dissolved in or suspended in the water.

(4) When bituminous sand is mixed with a small quantity of water, the concentration of substances which dissolve or are suspended in the water is greater than when a large quantity of water is used. The small quantity of water, after having been mixed with the bituminous sand, is a better wetting agent and displaces the oil from the sand more completely than is the case with a large quantity of water.

(5) Bubbles of air or of water vapor present in a system of water, mineral matter and small masses of oil, will become attached to the oil masses and will float them to the surface. However, only small bubbles a few millimeters and less in diameter are effective in floating the oil. Air and water vapor bubbles also become attached to and float mineral particles. Particles of minerals other than quartz are floated more readily than quartz.

(6) A clean and complete separation of oil from sand by the hot water process is impossible unless the natural packing of the bituminous sand is completely broken down and the oil is dispersed among the individual sand grains as small oil masses. The mineral particles and small oil masses must be free to move independently of each other under the influence of the small forces upon which the process depends.

The six statements were offered as the best summing up of the understanding of the bituminous sands and of the hot water process that could be made at the time. It was anticipated that the results of further work would lead to modifications of the statements. The formulating of them drew attention to what was imperfectly understood. One such matter was the wetting and oil-displacing characteristics of water containing dissolved or suspended substances. It was known that alkaline and acid substances dissolved in the water used for preparing a bituminous sand pulp for separation had an effect on the separation process and that adding clayey substances also influenced the process (1). But there was a strong suspicion that there was much to be found out about the role of clayey matter present in the bituminous sand itself. Recent work has shown that this suspicion was well founded. The purpose of this article is to report what has been observed about the role of very fine mineral matter in the separation process.

LABORATORY SEPARATION PLANT PROCEDURE

The laboratory separation plant in the Research Council of Alberta laboratories has been modified from time to time. Its present form is indicated in Figs. 1 and 2. The principal changes since the plant was last described (2) are the arrangement for flooding the bituminous sand pulp with the circulating stream of plant water and the method of maintaining the temperature of the plant water.

The circulating plant water system is a feature which the Research Council has used almost from the start of its studies of the separation process. The circuit is indicated clearly in Fig. 1. Plant water is pumped from the separation cell into the settling cone. The overflow from the cone passes into a constant flow regulator. Two streams leave this device. One stream, of constant flow, passes through a heater to the pulp-flooding cell and then on into the separation cell. The water in excess of the stream of constant flow escapes from the flow regulator by a second outlet and flows directly into the separation cell.

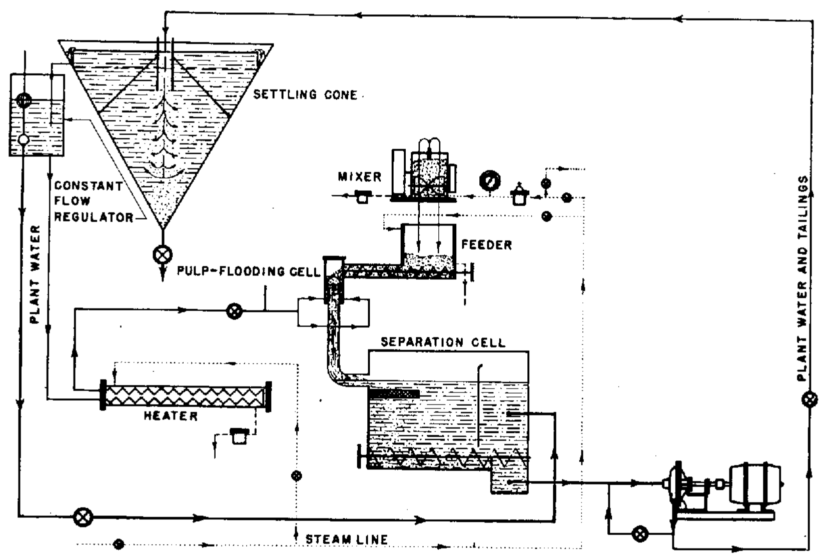

Fig 1—Diagrammatic drawing of laboratory separation plant showing the plant water circulation system.

Experimental separation runs are made on batches of bituminous sand of about 6.5 kgm. Conditions are varied to suit the study in hand. For what has come to be regarded as normal separation procedure, the batch of bituminous sand is put into the steam-jacketed Baker-Perkins Universal kneading and mixing machine and, after thorough mixing but before heating has commenced, a sample of the bituminous sand is taken for analysis. Distilled water amounting to about 10% of the weight of the charge is then added and the batch is heated to, and held at, 85°C during a period of 20 minutes. The bituminous sand pulp is dumped into the feeder. It pours readily. It is much like a thin brick mortar in nature and consistency. The feeder passes the pulp at a fairly constant rate into the pulp-flooding cell. The rapid, turbulent flow of hot water through this cell

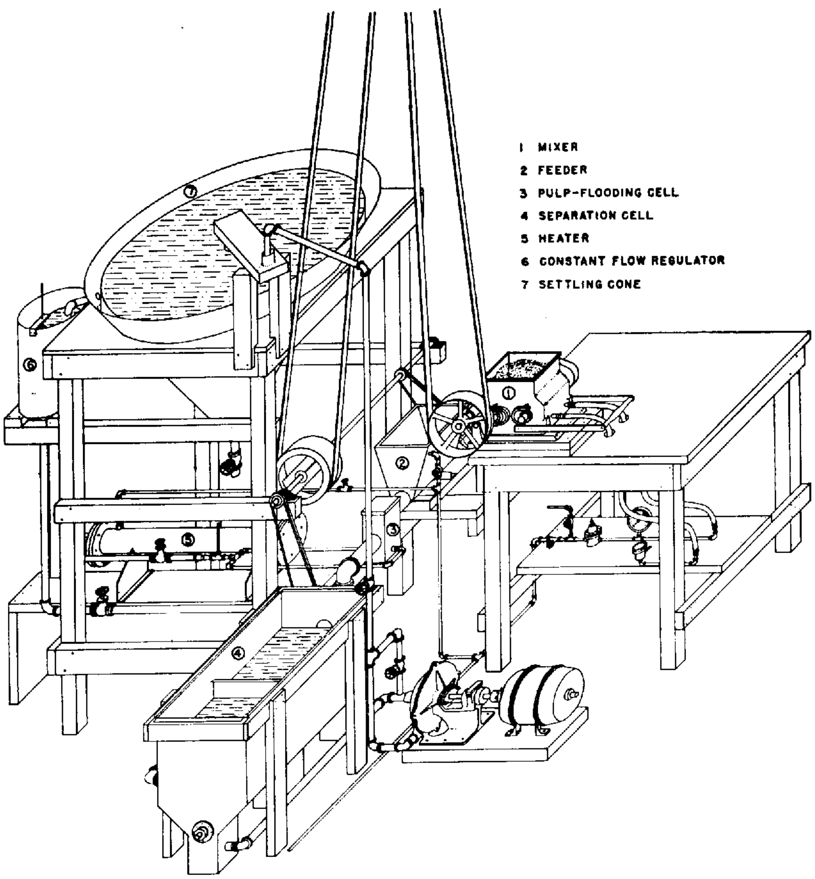

Fig. 2—Isometric drawing of laboratory hot water separation plant.

causes the bituminous sand pulp to disperse and to be swept through the overflow into the separation cell. Oil in the form of froth floats on the surface of the hot water in the separation cell while sand sinks and very fine mineral matter remains dispersed in the water. The sand is conveyed along the bottom of the separation cell by a screw conveyor into a boot. This boot is connected to the suction of a centrifugal pump. The sand, along with a stream of plant water, is pumped into the settling cone where sand as well as other finer material in the plant water sinks. Settled water flows back to the cell.

The circulation of water is continued after a batch of bituminous sand pulp has been run. The oil froth on the surface of the water in the separation cell is skimmed and is collected in a suitable container. While most of the oil froth forms at once on running the pulp into the circulating stream, a little more keeps forming as the plant water is kept circulating. A final skimming is done 20 minutes after the start of the run. Some froth appears on the surface of the water in the constant flow regulator. This is skimmed and is added to the other froth that has been collected.

The container holding the oil froth is weighed and then set aside to cool. During this interval the froth collapses and water is liberated from it, the amount varying with the type of bituminous sand being separated. It often is considerable. On stirring, the oil and liberated water separate and the water is poured off and weighed. The oil is then sampled for analyses. Besides oil, it contains mineral matter and a surprisingly large amount of water in spite of the liberated water that has been poured off.

The sand tailings and other material that settle in the cone are run out through the bottom valve. They may or may not be examined for oil content depending on the objective of the work under way.

It has been an aim of the Research Council to learn how to conduct the hot water separation process so that a maximum yield of oil of low mineral matter content will be obtained. As is to be expected, the yield and cleanliness of the oil vary since bituminous sand is far from being an aggregate of uniform composition. It is now known that the yield is affected by the clay content of the bituminous sand and decreases as the clay content increases. The general run of good grade bituminous sand gives a yield of from 75-85% of the oil content. The mineral matter content of the recovered oil falls between 5-10%, dry basis. It might be thought that the water content of the recovered oil as analysed after eliminating water which separates on collapse of the froth, would be erratic. However, it generally is about 35%. The analytical results reported in Table II are typical.

VERY FINE MINERAL MATTER IN BITUMINOUS SAND

The mineral aggregate of bituminous sand consists of sand particles, mainly quartz, ranging in size from 50-mesh and larger to minus 200-mesh and of other mineral matter of a clayey nature ranging in size from somewhat less than 200-mesh to colloidal dimensions. Determination of the size distribution of the mineral matter, from sand grains to particles of colloidal size, in the bituminous sand aggregate as well as in the mineral matter present in the various products of a separation experiment would be difficult and has not been attempted.. An indication of the content of clayey material has been obtained by determining the proportion of the mineral matter in question which remains in suspension after a period of one minute of settling. Such determinations are made on mineral matter from which oil has been removed by ignition in a muffle furnace. The ignited material is broken down in a mortar with a rubber-tipped pestle and is then dispersed in a beaker in warm water containing calgon. After allowing to settle for one minute, most of the water is siphoned off. More water with calgon is added and the dispersing, settling and siphoning is repeated. The whole set of operations is repeated until no more mineral matter is present in the siphoned water. The mineral matter which settles in one minute is dried, weighed, and subjected to sieve analysis. The mineral matter in the water that is siphoned off is determined by difference.

The fine mineral matter which does not settle in one minute is termed "clay". Admittedly, it is not clay in any strict sense. It is silt and clay without any indication of the proportions of these constituents. It is convenient to use the short term and, with the explanation given, there should be no misunderstanding. It is probable that it is the actual clay content of the so-called clay that is the important factor in affecting the separation process.

TEST MATERIAL FROM CLAY PARTINGS OCCURRING IN THE BITUMINOUS SAND DEPOSIT

Clay in the form of partings occurs in the bituminous sand beds. This clay appears to be quite free from oil although the clay is generally in small masses in association with oil-bearing sand. It is probable that the clay occurring in oil-free masses in partings is essentially the same material as the clay occurring as a constituent of an oil-impregnated sand.

Clay beds occur in the bituminous sand exposed in the cuts along the road leading to the Abasand Oils Ltd. plant on Horse River. A quantity of material was collected from two of these beds and was brought to Edmonton. In the laboratory, the material was broken up and dispersed in water. The dispersion was filtered through a 100 mesh sieve. The suspension passing through the sieve was divided into three fractions by settling. These fractions consisted of:

Fraction 1—material which settled during the time interval between 1 and 10 minutes.

Fraction 2—material finer than fraction 1 but which settled in 16 hours or less.

Fraction 3—material which was still in suspension after 16 hours of settling.

Fraction 1 contained some material belonging to Fractions 2 and 3. Fraction 2 contained some Fraction 3 material. A supply of the three fractions was stored in a wet, pasty form for experimental use.

ANOMALOUS SEPARATION RESULTS WITH BITUMINOUS SAND CONTAINING NO CLAY

A disturbing experience directed attention to the significance of clay present in a bituminous sand as a natural constituent. Oil Sands Ltd. operated its separation plant during the summer of 1944 and events were indicating that there was likelihood of an agreement between this company and the Government of Alberta regarding pilot plant studies. Since the Council might become involved in pilot plant work at Bitumount, the desirability of having bituminous sand from there for laboratory work was obvious. Consequently opportunity was taken to collect a supply of sand from the bottom part of the Oil Sands Ltd. quarry where material was being excavated by bulldozer and dragline for feed to the separation plant. The supply was sent to Edmonton and was used in laboratory studies. The outcome, as indicated, was disturbing. Separation results on this supply of bituminous sand was bad. The yield of oil was very low and the oil that was floated as froth was very sandy. The Council thought it understood bituminous sand separation and knew how to carry out the hot water process efficiently. Yet its procedure failed lamentably with the very bituminous sand that, probably, it would be called upon to deal with in pilot plant operations.

The experience was interesting as well as disturbing, for bituminous sand had been taken from the Oil Sands Ltd. quarry at several times in the past and these supplies had given excellent separation results in the laboratory. On the next visit to Bitumount further supplies were collected. This time the bituminous sand beds exposed in the quarry face were divided into upper, middle and lower sections of about eight foot thicknesses and a fourth section was established at a still lower elevation in another location in the quarry. Material was collected from each section separately. Laboratory runs were made on each supply. Results were very good with the bituminous sand from the upper and middle sections; they were poor with the lower section; and they were bad with the fourth lowest section.

Examination of the compositions of the four supplies of bituminous sand revealed one feature of difference that held promise of being the significant one. There were variations in the amount of very fine mineral matter in the four sands which paralleled the variations in separation results. Sieve analyses of the mineral aggregates of the four sands showed that material passing the 200-mesh sieve was 7.5% in the case of the upper bituminous sand, 5.3% for the middle sand, 1.5% for the lower sand and 1.0% for the fourth sand. The bituminous sand from the upper and middle sections gave nomal yields of oil froth of low sand content in separation tests; the yield was good but sandy for the lower section; the fourth bituminous sand gave a very small yield of sandy oil.

Material passing the 200-mesh sieve consists of very fine sand, silt and clay. Of these three constituents, clay was the one to suspect as being significant. The inference was that addition of clay to the bituminous sands that contained little material passing the 200-mesh sieve should affect separation behaviour favorably. Consequently runs were performed on the fourth sand supply in which additions of the Clay Fraction 3 described in the previous section were made to the bituminous sand. Addition of 0.5% of this clay caused the yield of oil as froth to rise to over 80% and for the sand content of the froth to fall to about 15%, dry basis. Additions of 0.25% and 0.1% of the clay gave yields of 80% oil but the sand contents of the froths rose to 25% and 35% respectively. Additions of more than 0.5% of the clay caused progressive falling off of yield. Additions of Clay Fraction 1 were made but as this fraction contained some material belonging to Fraction 3 it was not considered that results were signficant. Good yields of a sandy froth were obtained when 1% of Clay Fraction 1 was added.

The marked improvement in separation results which accompanied addition of Clay Fraction 3 to a bituminous sand which contained very little natural clay, along with good separation results with bituminous sands which had a considerable natural clay content pointed strongly to an important role for clay in the hot water separation process. It appeared that some clay in the bituminous sand was necessary for normal response to the process. This was a new idea. It was known that a clayey bituminous sand gave a poor yield of oil (1).

A further observation may be recorded here. A mixing time of 20 min. had become customary in preparing bituminous sand pulp for separation. This was a convenient time when a series of runs was being put through. During the study of the difficulty with the separation of the bituminous sand under discussion, increasing the mixing time to 180 min. was tried. Whereas with 20 min. of mixing and no addition of clay the yield of oil was often too small to collect for analysis, the long period of mixing resulted in a yield of 90% of oil froth. The sand content of the oil was high—about 30%, dry basis. Increasing the time of mixing the pulp for a bituminous sand which separated normally had no effect on separation results. They were neither improved nor impaired.

Probably it should be commented that a bituminous sand bed that contains little material passing the 200-mesh sieve and consequently very little clay is a rare occurrence. The tendency is decidedly in the other direction. The practical problem will be to deal successfully with bituminous sand containing too much rather than too little clay.

THE ASSOCIATION OF OIL WITH MINERAL MATTER IN THE TAILINGS AND PLANT WATER OF THE LABORATORY SEPARATION PLANT

Experience with separation runs on bituminous sands in general had shown that from 75 to 85% of the oil present in the bituminous sand was recovered in the form of oil froth. The yield was constant for any one supply of sand but varied for sands from different locations or with different storage histories. What became of the oil which did not float as froth was a matter of interest and importance. Consequently a series of runs on a number of bituminous sands from different locations was made to account for all the oil in each run.

The separation runs were conducted as described in a former section except that a pulping time of 45 min. was used. The longer period could do no harm and might do good in the case of some of the bituminous sands of the series. The oil froth floating on the separation cell a short time after all the pulp had been fed was skimmed. The plant water circulation was not stopped. After an hour and a quarter of circulation the small amount of froth that had collected on the water surfaces in the separation cell and in the constant flow regulator was skimmed and was added to what had already been collected.

At the conclusion of the run the sand tailings were drawn from the bottom of the settling cone into a pail. These tailings were separated into sand and clayey material in the following manner. About 500 gm. of tailings were put into a 2-liter beaker along with an approximately equal volume of water. The tailings and water were stirred mechanically for one minute. Stirring was stopped. At the end of a 15 sec. settling period the water with the material still suspended in it was poured off. The sand remaining in the beaker was stirred with more water which was poured off after settling for 15 sec. The sand was washed four times in this way. It was then spread out to air-dry. The water suspensions that had been poured off were stirred up and, after settling for one minute, the suspension was siphoned off. Water was added to the material remaining in the beaker, stirred, settled and siphoned off. These operations were repeated four times to remove all clayey material from the small residue of coarse material. This latter material was collected separately. It made up part of what is termed "miscellaneous" in Table II. All the tailings drawn from the settling cone were worked over in the manner described. The clayey suspensions settled clear overnight and the clear water was siphoned off. In this way bulk was kept to manageable dimensions. A clayey suspension containing all the clayey material was got into a 2-liter beaker eventually for drying in an oven, weighing and analysis.

The plant water in the settling cone was left to settle for two days after drawing off the sandy tailings. The clear water was siphoned off and settled material was removed through the bottom valve into a pail. These settlings were separated into clayey material and a coarser miscellaneous residue in the manner described. From the volume of water in the cone and the weight of settlings collected from it, the weight of settlings in water in the rest of the plant was obtained by calculation.

The oil contents of the sandy and clayey portions of the tailings after drying, were determined both by extracting with benzene using a Rotarex centrifugal filter and by igniting in a muffle furnace. The methods checked closely with sand tailings but deviated with clayey material. The extraction method gave too low results with clayey matter because of the impossibility of extracting all oil from the clay even with numerous extractions. The ignition method gave too high results because of loss of water of hydration. The mean of the results from the two methods was used in calculations.

The bituminous sands used in this series of experiments came from several locations in the bituminous sand area. One sample was collected from the quarry of Abasand Oils Ltd. on Horse River in the southern part of the area near McMurray. Another sample came from Ells River at a point northwest from Fort MacKay. The remaining samples came from Bitumount. These were taken from different elevations in the sixty feet of beds exposed at that location. The Bitumount bituminous sands are numbered in the order of increasing depth of occurrence. The various locations mentioned are shown on the map, Fig. 3.

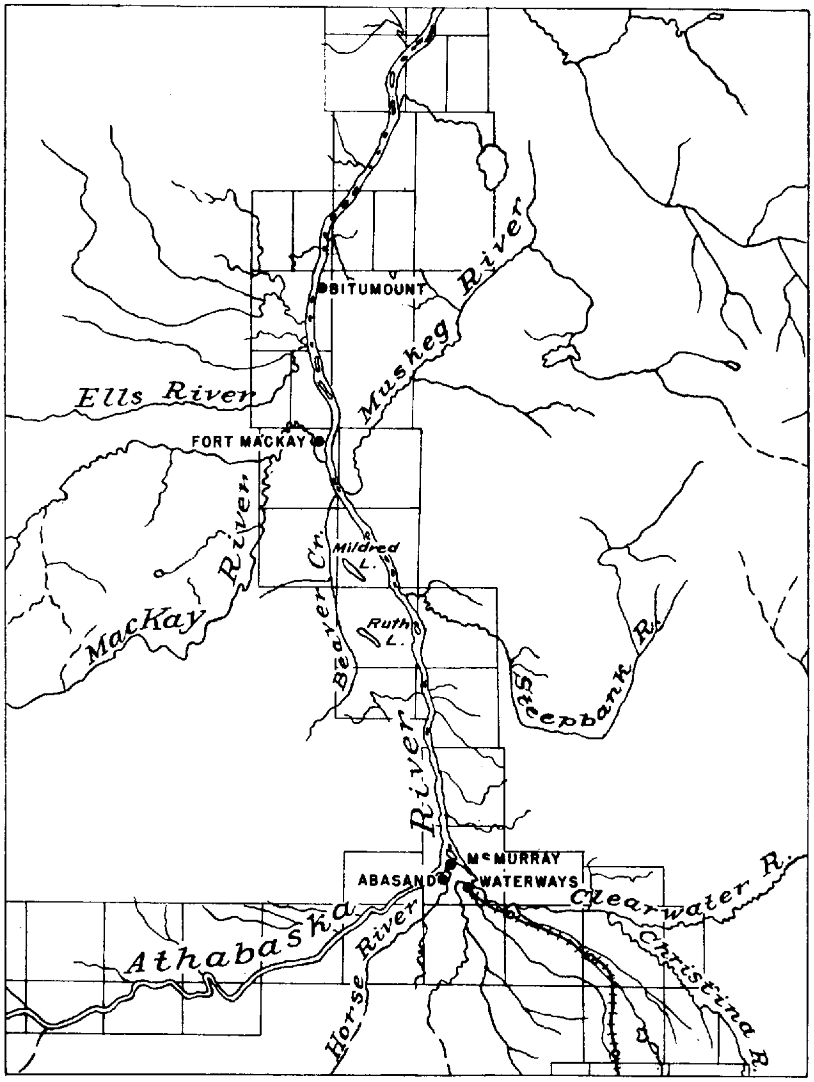

Fig. 3—Map of the bituminous sand area along the Athabaska River showing locations of places of interest.

The nature of the bituminous sands used is shown by their analyses recorded in Table I. The sands are arranged in the table in the order of increasing clay content. What became of the oil when these sands were put through the hot water separation process is shown by the data of Table II.

TABLE I

Compositions and Sieve Analyses of Bituminous Sands Used in Separation Runs for Accounting for All Oil

Bituminous Sand	Bitumount No. 2	Bitumount No. 4	Abasand	Bitumount No. 3	Bitumount No. 1	Ells River	Bitumount No. 3 + Clay*
Composition:							
Water, %	1.0	4.5	3.1	3.1	2.1	4.5	
Mineral matter, %	84.7	84.8	81.7	81.4	82.8	84.1	
Oil (by difference), %	14.3	10.7	15.2	15.5	15.1	11.4	
Sieve analysis of mineral matter after ignition:							
Retained							
on 50 mesh, %	11.0	41.2	0.3	13.0	18.3	0.2	
" 80 " %	46.8	34.3	3.3	41.0	49.9	3.5	
" 100 " %	20.8	10.2	17.9	20.0	13.3	14.5	
" 200 " %	16.4	9.0	69.9	18.5	11.0	61.0	
Passing 200 " %	5.0	5.3	8.6	7.5	7.5	20.8	
Mineral matter still suspended in water after 1 minute settling, %	3.5	4.0	4.0	5.7	5.7	7.4	16.8 (calc.)

*The clay added weighed 11% of the weight of the charge of bituminous sand. The clay consisted of 50% of Fraction No. 1, 25% of Fraction No. 2 and 25% of Fraction No. 3.

TABLE II

Distribution of Oil Between Oil Froth, Sand in Tailings, Clay in Tailings and Plant Water in Separation Runs to Account for All Oil

Bituminous Sand	Bitumount No. 2	Bitumount No. 4	Abasand	Bitumount No. 3	Bitumount No. 1	Ells River	Bitumount No. 3 + Clay
Composition of oil froth:							
Water, %	35.4	37.8	27.7	35.7	36.4	36.5	35.4
Mineral matter, %	4.5	2.8	4.7	3.9	5.8	3.9	3.8
Oil (by difference), %	60.1	59.4	67.6	60.4	57.8	59.6	60.8
Oil content of sand tailings (dry basis), %	0.50	0.41	0.44	0.27	0.56	0.25	0.41
Oil content of clay in tailings and in plant water (dry basis). %	52.8	43.5	47.4	44.8	41.8	42.2	35.0
Percent of total oil found in:							
Oil froth, %	78.6	76.1	77.1	80.3	79.4	63.4	44.2
Sand tailings, %	2.7	3.0	2.1	1.3	2.9	1.6	1.2
Clay in tailings and plant water, %	13.3	17.1	15.4	14.9	12.1	31.4	52.4
Miscellaneous, %	2.7	1.6	4.1	1.6	2.2	2.1	1.6
Total oil accounted for, %	97.3	97.8	98.7	98.1	96.6	98.5	99.4

All the bituminous sands used in this series of experiments separated in a normal fashion. Consequently the analyses, Table II, of the oil froths obtained are typical. Note how the water content holds closely to 35% for froths given by sands from Bitumount and Ells River. The froth from the Abasand sand has a lower water content. This sand is far removed from the others in location and it contains a much more viscous oil. The mineral matter contents of the froths are variable but low.

The most striking figures in Table II are those showing the high oil content of the clayey material which was separated from the tailings and plant water. Here, obviously, is where oil that does not float as froth, goes. The oil content of the actual sand in the tailings is low. It is not improbable that even this low content is due chiefly to clayey material that adhered to them in spite of the thorough washing they received.

As the clay content of bituminous sand goes up, the yield of oil froth comes down. The data of Tables I and II support this statement in general although not in detail. The yields of oil froth from the Abasand and Bitumount bituminous sands do not follow the rather small variations in content of so-called clay. However, in the cases of Ells River sand and of Bitumount No. 3 plus clay where there was an undoubtedly marked increase in clay content, the yield of oil froth dropped sharply.

There can be no doubt that the oil which fails to float as froth in a separation run becomes associated with the clayey material dispersed in the plant water. How is it associated? It would be natural to suppose that the oil is distributed over the surfaces of the clayey particles. Visual inspection of the clayey material indicates that this view is not correct, however. This material is seen to contain many small black particles. Evidence will be presented in the following section which indicates that these black particles are flecks of oil containing variable amounts of clay. These tiny oil flecks disperse in the plant water along with clayey matter and, when the plant water is allowed to settle, the oil flecks settle along with the clayey material.

CLAY CONTENT OF OIL FLECKS

Since the dark flecks of, presumably, oily material could be seen in the fine mineral matter washed out of the sand tailings or settled from the plant water, steps were taken to collect these particles and to examine their composition. Such examination was made for a number of separation runs. Results were similar. One case will serve to indicate the findings.

A separation run was put through in the usual manner. The clayey material was washed from the sand tailings and was recovered in the form of a concentrated water suspension as described in the previous section. Portions of this suspension were taken and were diluted with distilled water. This suspension was heated in a beaker. When the temperature reached 65° C a stream of air bubbles was released into the suspension. The bubbles were formed by passing slightly compressed air through a porous disc. Oil froth collected on the surface of the water as the temperature rose slowly to 90° C., the froth being collected at various temperatures and analysed. Different portions of the clay suspension were treated in this manner in water containing various reagents.

The use of air bubbles in connection with forming an oil froth may give the impression that the oil flecks were collected by the air bubbles and were floated by them to the surface. Whatever may have been the idea behind using the air bubbles, they did not collect the oil flecks. As far as could be observed, they served only to stir the suspension in a particular fashion. The stirring brought oil flecks to the surface of the water. The form of agitation resulting from the rising bubbles caused a wash to rise up the side of the beaker a short distance above the surface and to fall back. Oil flecks that got caught in this wash tended to film out on the surface of the water. It seemed that the froth was built up from oil reaching the surface in this way. The nature of the stirring seemed to be related to the nature of the oil flecks that would film out on the surface. For instance, when sand was put on the bottom of the beaker to cause bumping along with the stirring by bubbles, the mineral content of the froth was increased. And this increased content was clay—not sand.

TABLE III

Contents of Mineral Matter in Oil Froths Formed by Floating Oil Flecks from Clayey Material Separated from Tailings. Various Reagents Added to Suspensions of Clayey Material

Suspension Medium	Temperature	Oil Froth			
		Stirring with air bubbles		Stirring with air bubbles and bumping	
	°C	Mineral content* (dry basis) %	Recovery of oil as % of oil in bituminous sand	Mineral content* (dry basis) %	Recovery of oil as % of oil in bituminous sand
Water	65-90	15.0	15.8	21.3	28.3
0.063% calgon in water	"	8.8	7.1	10.5	10.9
0.063% sodium carbonate in water	"	7.9	7.6	15.4	16.5
0.035% sodium hydroxide in water	"	8.5	4.5	14.7	14.3
0.050% sulphuric acid in water	"	19.0	32.6	26.2	34.7

*Froth was removed a number of times as the temperature rose. Its mineral content increased as the temperature rose, in general. The mineral content figures in the table are weighted average values and were determined by ignition, no correction being made for loss of water of hydration.

Table III shows the clay contents of the froths formed under various conditions from oil flecks present in the clayey material in the tailings from a separation run on Ells River bituminous sand. These data are consistent with the view that the oil which fails to float as froth in the separation cell and which remains dispersed in the plant water along with the sand and clayey material is in the form of oil flecks which have a considerable content of clay. This content varies from some fairly critical minimum value to high values. This minimum value is also the maximum value for the clay content at which oil flecks will join the froth under conditions existing in the separation cell. When the oil flecks are exposed to conditions which are more favorable to getting them onto the water surface as froth, as in the beaker experiment, more of the flecks of a higher range of clay content float. Increasing the temperature under a given condition of agitation and stirring increases the range of clay content. Acid conditions also increase it. On the other hand, alkaline conditions decrease it.

Under any given condition of temperature, hydrogen ion concentration, agitation, etc., the oil flecks of clay content such that these flecks can film onto the water surface readily, do so without undue delay. But there seems to be no end to the froth that appears on the water. A little keeps forming indefinitely. And the clay content keeps increasing as time goes on. It seems that at long last a fleck of very high clay content gets to the surface in such a way that it will stay there. Small quantities of froth with a clay content of 70% have been collected and examined.

THE ROLE OF CLAY IN OIL FLECK FORMATION

When a bituminous sand which separates normally is mixed and heated with water in preparation for separation, the oil is present in the pulp as oil flecks lying among the sand grains. A bituminous sand which contains practically no clay does not respond properly to the separation process. This would make it appear that oil fleck formation is part of the mechanism of the separation process and that clay is necessary for the formation of oil flecks. Some support for this idea was given by experiments in which dry, clean separated oil was dispersed into flecks by agitation with clay suspensions.

The oil for these experiments was obtained by cleaning and drying the crude oil produced by the Oil Sands Ltd. separation plant in 1944. The wet oil was settled at 85° C for 24 hours to remove sand particles. The settled oil was then pumped through a heater in which its temperature was raised to 155° C. This heating converted the wet oil into an oil-steam foam. The steam was removed in a separator. Approximately 3% of light ends were carried out of the oil by the steam. The dried oil contained 2.9% of clayey mineral matter.

Ten grams of Clay Fraction 3 were dispersed in 200 cc of distilled water and the suspension was heated to 85° C. While the suspension was being stirred mechanically with a glass paddle, 15 gm. of warm oil were poured into it. The stirring caused the suspension to swirl in the beaker; there was not much agitation. The stirring was stopped after several minutes and the suspension was examined. It was observed that the oil had all gone into flecks. Also, the clay suspension had gelled and the oil flecks were held in the gel. Several additional 15 gm. lots of oil were stirred into the suspension and these also dispersed into flecks. Clay suspensions containing 5 gm. and 2.5 gm. of clay in 200 cc of water dispersed oil into flecks but the resulting clay gel was not strong enough to prevent the flecks from settling when the stirring was stopped.

A suspension of Clay Fraction 1 did not cause the oil to disperse into flecks. The oil collected into round beads which settled on stopping the stirring but which did not coalesce.

A suspension of Clay Fraction 2 caused some of the oil to disperse as flecks. The rest of it floated as a heavy froth when stirring was stopped.

In the case of the suspension of Clay Fraction 3 in which oil was dispersed as flecks, diluting and stirring with water containing calgon caused the clay gel to peptise and the oil flecks to settle. By repeatedly diluting and siphoning off the clay suspension after settling, it was possible to obtain a quantity of oil flecks. Analysis of these flecks showed that their mineral content was very little greater than that of the oil which was dispersed. Oil flecks which become dispersed in the plant water during the separation of a bituminous sand have clay contents which vary up to high values.

The experiments described support the idea that clay in a bituminous sand is necessary for prompt fleck formation and that it is the actual clay in the so-called clay that is the active agent.

The differences in the effects of the three clay fractions on the dry oil are interesting. Fraction 1, which would consist mainly of silt, caused the oil to disperse into round beads which settled to the bottom without coalescing. Fraction 3 which would consist of real clay extending into colloidal material, caused the oil to disperse into small flecks which remained dispersed in the suspension Fraction 2 which would consist of fine silt grading into clay caused the oil to form some flecks, but when stirring was stopped most of the oil was found on the surface of the suspension as a froth. It would seem that the intermediate clay fraction caused an intermediate form of dispersion of the oil and that it is this intermediate form of oil dispersion that has the least difficulty in getting onto the water surface, filming out on it and forming froth.

WEATHERED BITUMINOUS SAND

Everyone who has experimented with the recovery of oil by the hot water method has found that bituminous sand deteriorates after it is removed from the deposit. Best satisfaction is got from separation runs on freshly mined sand. Runs performed on sand in storage get progressively more disappointing as time passes. Just what happens to the bituminous sand is not known. The lack of knowledge is evaded by saying that the bituminous sand weathers, or oxidizes, or dries out. Research Council workers have thought that the deterioration was due to loss of the natural water content of the bituminous sand or to the disappearance of the water films separating the oil from contact with the sand surfaces thus allowing the oil to become directly attached to the sand. Consequently they have been at pains to bring supplies of bituminous sand from the north to Edmonton in tightly covered cans or even in glass sealers in order to preserve the natural moisture content. However, information has come to light which indicates that the deterioration is connected with the clay content of the bituminous sand and with its association with the oil. It appears that the change in association between clay and oil can take place without loss of water from the bituminous sand.

The Bitumount No. 3 and the Ells River bituminous sand supplies used for the material balance experiments reported in Table II were collected from the deposits in the north during July 1947 and were used in the laboratory in Edmonton early in August 1947. The Bitumount No. 3 sand was placed in a carbide can with a well-fitting lid as it was removed from the deposit. The Ells River sand was placed in half-gallon glass sealers equipped with rubber rings. The two supplies were stored in the laboratory. It had been the practice to keep bituminous sand supplies out-of-doors but the array of cans and boxes alongside the building had become objectionable. Storage at the higher indoor temperature instead of out-of-doors may have had an accelerating effect on the deterioration of the bituminous sand from the standpoint of separation.

Sand was taken from these two supplies during April 1948 for separation runs. The results of these experiments along with former results obtained when the supplies were comparatively fresh are given in Table IV. It can be seen from the data that there was a marked increase in the mineral matter content of the oil froth separated from the stored bituminous sands. The yield of recovered oil from Bitumount No. 3 was not affected by the storage. But the yield of oil from the Ells River sand was greatly decreased.

TABLE IV

Results of Separation Tests on Bitumount No. 3 and Ells River Bituminous Sands Performed when the Bituminous Sands were Fresh from the Deposit and After Eight Months in Storage.

Bituminous Sand		Bitumount No. 3		Ells River	
		Fresh	Stored	Fresh	Stored
Composition of bituminous sand:					
Water,	%	3.1	2.1	4.5	4.7
Mineral matter,	%	81.4	83.1	84.1	84.3
Oil (by difference),	%	15.5	14.8	11.4	11.0
Composition of oil froth:					
Water,	%	35.7	32.7	36.5	37.2
Mineral matter,	%	3.9	14.1	3.9	6.6
Oil (by difference)	%	60.9	53.2	59.6	56.2
Mineral matter (dry basis),	%	6.1	20.9	6.2	10.6
Oil recovered as froth,	%	80.3	83.0	63.4	36.5

TABLE V

Mechanical Analyses After Ignition of Mineral Matter Retained by Oil Froths in Separation Runs on Fresh and Stored Bituminous Sands.

Bituminous Sand	Bitumount No. 3		Ells River	
	Fresh	Stored	Fresh	Stored
Content of mineral matter in 100 gm. of dry oil froth:				
Retained on 50 mesh. gm.	0.5	0.3	0.3	0.2
" " 80 " "	1.4	1.4	0.5	0.5
" " 100 " "	0.7	1.1	0.3	0.3
" " 200 " "	1.0	2.8	1.4	1.1
Passing 200 " "	1.9	13.0	3.1	7.0
Mineral matter still suspended in water after 1 min. settling, gm.	1.8	10.6	3.0	4.8

Incidentally, the data of Table IV give evidence of an interesting phenomenon. As bituminous sand rests in storage in a container, a portion of the oil may drain slowly downwards through the sand. The oil is viscous and it is easy to suppose that movement of oil through the sand under the influence of gravity would be negligible. However, when Bitumount No. 3 was used in the laboratory shortly after it was collected, the whole carbide can of it was removed from the can and was well mixed. The oil content of a charge for a separation run, taken from the whole lot, was 15.5%. When a separation run was made on this sand after eight months of storage, a charge was removed from the upper part of the sand remaining in the can. The oil content of this charge was 14.8%. A second charge taken from lower down in the can had an oil content of 16.9%. This effect does not show up in the case of the Ells River sand. This sand was stored in half-gallon sealers and all the contents of three sealers went into a charge. The effect happens in the sealers however and to offset it in work where it matters it has been found necessary to turn the sealers upside down every day. The effect can be observed in the bituminous sand beds in the deposit. Where a considerable thickness of bituminous sand occurs between clay partings, the upper part of this bed is lean whereas the lower part is well saturated with oil.

Returning to the topic in hand, it has been noted that the mineral content of the recovered oil was increased as a result of storage. What is the nature of the mineral matter that has increased this content? Table V shows that it is mainly material passing 200-mesh and that much of this fine material is clay.

It appears that deterioration of bituminous sand in storage, from the standpoint of hot water separation, is accompanied by a change in the association of oil and clayey material. Possibly the clay tends to pass out of the water phase into the oil phase. It is difficult to offer an explanation of why the yield was lowered in the case of the Ells River sand and not with Bitumount No. 3. However in Ells River bituminous sand the ratio of mineral matter passing 200-mesh to bitumen is 190:100 by weight whereas in Bitumount No. 3 bituminous sand the ratio is 48:100. The presence in Ells River bituminous sand during storage of such a large proportion of fine material relative to the oil could enable the association of sufficient fine material with the oil so that the oil flecks formed during the pulping operation were not able to float as froth in the separation cell, thus decreasing the yield.

SECONDARY RECOVERY OF OIL FROM TAILINGS AND PLANT WATER OF A SEPARATION PLANT

The recovery of oil as froth in the hot water process is about 80% for good grades of bituminous sand containing some but not too much clay. The yield decreases as the clay content increases. Consequently clayey bituminous sands are unsatisfactory for processing in a hot water separation plant unless the yield of oil as froth can be augmented by further recovery of oil from the tailings and plant water. A further operation which would increase the overall yield of oil from good grades of bituminous sand to more than 80% and which would bring the yield from clayey sands to a similar percentage is desirable.

An attempt has been made at several bituminous sand plants to recover further oil from tailings. In each case the procedure has been to add a second separation cell and to wash the tailings from the first cell into it. And in each case the experience has been that so little additional oil was won that the extra cell was not considered worth while.

In the light of results given in this report a rather different method for getting secondary recovery is indicated. The first step would be to separate tailings material into sand and slimes. The sand would contain very little oil and would be run to waste. The slimes would contain the flecks of oil on which secondary recovery would depend. These slimes could be treated in some form of flotation cell which would cause the oil flecks to form a froth. By careful control of flotation conditions it should be possible to recover only those oil flecks with not too high a clay content for a useful oil product. The indication is that the lower the clay content an oil fleck has, the easier it is to cause it to float. It is probable that an increase in yield of 5-10% could be obtained in this way with even quite good grades of sand. The secondary yield might be very important with clayey bituminous sands.

REVISED STATEMENTS

The information reported in this article and other information that has been obtained make it necessary to revise the statements summarizing present knowledge about the bituminous sands and their reactions when treated with water as in the hot water separation process. The revised statements are:

(1) Bituminous sand is an aggregate of sand, clayey matter, oil and water. The sand consists mainly of quartz particles of 50 to 200-mesh size and smaller, but also of particles of other minerals including mica, rutile, ilmenite, tourmaline, zircon,

spinel, garnet, pyrite, and lignite. Clay occurs interbedded with the bituminous sand and is also a normal constituent of the bituminous sand itself. Ironstone nodules of all sizes up to eight inches in diameter occur in the bituminous sand beds, especially in the southern part of the deposit. The oil is viscous, naphthenic and of a specific gravity slightly greater than that of water. The oil content ranges up to, and sometimes exceeds 17% by weight. Rich bituminous sand from beds not invaded by water have a water content of 3 to 5% by weight. Some of the water is present as films on sand grains separating the oil from direct contact with the sand surfaces. Rich-looking bituminous sand is practically saturated with oil and water, differences in oil content being due mainly to differences in porosity of the mineral aggregate. The viscosity of the oil in the southern part of the deposit is many times greater than that of the oil in the northern part causing marked differences in the firmness of oil cementation of the bituminous sand beds in the two areas (3). The formation temperature of the bituminous sand deposit is about 36°F. (4) *

(2) Water wets quartz and other siliceous minerals more readily than does mineral oil. Consequently, when bituminous sand is mixed with water, the already existing separation of oil from sand surfaces by water is at least preserved, and may be extended if not already complete.

(3) When bituminous sand is mixed and heated with water into a mortar-like pulp, the oil is dispersed into small oil flecks which lie unattached among the sand grains. The content of clayey material in bituminous sand plays an important role in fleck formation and fleck formation plays an important role in the hot water separation process. In the rare cases of bituminous sands containing practically no clay, the separation process proceeds unsatisfactorily.

(4) The oil flecks present in a bituminous sand pulp vary in size and in the amount of clayey material that is associated with them. As the clay content of bituminous sand increases, the amount of clay associated with the oil flecks increases.

(5) When a hot bituminous sand pulp is flooded with hot water under conditions of agitation and access to air, oil flecks of low clay content gather together into a froth. This froth occludes or otherwise retains sand particles in amount depending on conditions. Particles of minerals other than quartz are retained more readily than are quartz particles. Oil flecks of high clay content are not gathered into the froth and remain dispersed in the sand and water. The clay content which determines whether an oil fleck will go with the froth or not varies with conditions but is in the neighborhood of 10%. Oil flecks which become dispersed in the water can be induced to form froth by submitting them persistently to conditions which bring the flecks in contact with the water-air interface.

*A direct reading of formation temperature was made by lowering, in wintertime, a maximum thermometer to a depth of 150 feet down a mud-filled drill hole in the Mildred-Ruth Lake area. The reading was 36°F. This observation was accomplished through the co-operation of Mr. H. C. Spaetgens, Refinery Superintendent, Abasand Oils Ltd.

(6) Satisfactory separation of oil from sand by the hot water process is impossible unless the natural packing of the bituminous sand is completely broken down in the pulping operation and unless the pulp is subsequently dispersed in excess water. The mineral particles and oil flecks must be free to move independently of each other under the influence of the small forces upon which the process depends.

ACKNOWLEDGEMENT

The authors wish to record their indebtedness to Mr. S. J. Groot, Draftsman-Compiler, Research Council of Alberta for the drawings appearing in this article.

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