TRIALS OF RECOVERY AND CLEANUP TECHNIQUES ON BITUMEN DERIVED FROM ORIMULSION

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ABSTRACT: *Orimulsion is the trade name for a fine, bitumen-in-water emulsion produced in Venezuela by Bitor S.A. However, when it is spilled in seawater, its dispersibility does not always prevent bitumen from resurfacing as films or patches. The physical properties of the material that resurfaces (i.e., viscosity and cohesiveness) are a function of those of the natural bitumen from which Orimulsion is prepared and represent a serious challenge for oil spill response.*

To address manufacturers' and operators' concerns about dealing effectively with such a spill, trials were organized by Cedre at its test facilities on behalf of Bitor Europe Limited and SK Power and National Power and with the participation of OSRL. The aim was to test recovery and cleaning processes to cope with bitumen originating from a spill of Orimulsion. The trials recreated a bitumen pollution incident on a Cedre lagoon and artificial beach and evaluated various recovery and cleanup equipment.

The tests showed that there is no one collecting or cleaning device that can be recommended to the exclusion of all others. Instead, different options have been highlighted, depending on the various forms that bitumen can take (films, patches, tar balls, "tea leaves"), its state (fresh or weathered), and the shoreline substrates.

On water, skimming and pumping a slick of bitumen is generally difficult because of the cohesive nature and the high viscosity of the product. On the other hand, a trawl net managed to collect bitumen lumps floating on the lagoon and accumulated them into a disposable sock.

On the shore, mechanical screening proved successful in recovering weathered bitumen on the artificial sand beach. Manual collection is also efficient when bitumen forms cohesive slicks. Pressure cleaners removed bitumen from hard surfaces when accumulations were first scraped off and a cleaning product was applied. Coated pebbles could be cleaned by mixing them with solvent in a cement mixer; recommended cleaning agents were petroleum cuts with low aromatic content. Contaminated sand could also be washed using a scrubbing machine.

Overall, these trials proved that solutions exist to cope with a spillage of Orimulsion bitumen. Operational conclusions were drawn that incorporated bitumen fate, shoreline types, and logistic considerations.

Background

Orimulsion is a hydrocarbon product made up of bitumen produced in the Orinoco region of Venezuela and marketed in Europe by Bitor Europe Ltd., subsidiary of Bitúmenes Orinoco, S.A., itself a subsidiary of the Venezuelan oil company Petróleos de Venezuela, S.A. For handling and transportation purposes, the bitumen is processed into a fine, oil-in-water emulsion containing 70% bitumen for 30% water and is stabilized by a surfactant, nonyl phenol ethoxylate, at approximately 0.2%. The product thus obtained, Orimulsion, can be burned as such in the power utilities of the heavy industrial sector. This fuel is relatively recent to the marketplace; the first commercial delivery took place in 1989. Because it is cost-competitive compared with coal, its marketing strategy is directed especially toward operators of oil-fired power stations that are planning to convert to coal or to build new coal-fired stations.

In Europe, several sites have already adopted Orimulsion, and there are others that are contemplating conversion to this new fuel. For example, SK Power is currently firing Orimulsion at its Asnaes power station in Denmark, and National Power is considering converting a Pembroke power station in Wales to run on Orimulsion. Bitor Europe Ltd., as the marketer of Orimulsion, and SK Power/National Power, as actual or potential customers, all recognize the importance of being able to deal effectively with a spill of Orimulsion. These trials were seen as a means of addressing this concern.

Since it is a bitumen-in-water emulsion, Orimulsion displays particular physical properties. It has a strong dispersibility; since water is the continuous phase, a spill in seawater would result in the immediate dispersion of the product in the first meters of the water column. However, in a confined area and if agitation remains low, the bitumen droplets can recoalesce and reproduce the original bitumen in the form of films, slicks, patches, or tar balls drifting at the water surface and are able to deposit on the shoreline or any man-made structure. A spill of Orimulsion is thus likely to be a combination of a subsurface dispersed phase and a surface cohesive bitumen phase.

Modeling and testing work has already been done to monitor and, as far as possible, control the subsurface dispersed phase (Gunter and Sommerville, 1991; Jokuty *et al.*, 1995; Gunter *et al.*, 1995); however, much less is known about the behavior and fate of the bitumen surface phase. From a practical viewpoint, the bitumen phase is also the one for which most response action can be undertaken, either by recovery (at sea or onshore) or by cleanup. These trials therefore focused on the best ways and means to recover and clean up the bitumen originating from an Orimulsion spill.

Aim of trials

The principal objectives of these trials were to assess different recovery and cleanup techniques used on the bitumen when it is free-floating on water or deposited on various shoreline habitats (rocks, pebbles, sand) and man-made structures (concrete wharves, wood and metal plates, boat hulls).

Regarding recovery on water, the precise objectives were as follows:

- Test skimmers designed for the recovery of very viscous oils
- Test a specially designed trawl net
- Assess the suitability of other recovery means: manual collection in shallow waters, use of sorbents, etc.

On the shoreline, selective recovery of bitumen can be envisaged prior to cleanup operations, and the efficiency of the following was evaluated:

- Mechanical screening of weathered patches of bitumen and tar balls deposited on sand
- Manual collection

Regarding beach cleanup, the different shoreline types were split into three categories on which different actions could be undertaken and evaluated:

- Rocks: scraping, high-pressure hot water jetting, use of solvents
- Pebbles: high-pressure hot water jetting, removal and cleanup in cement mixer, use of solvents
- Sand: scrubbing machine

Regarding man-made structures and equipment cleanup, the objectives were to assess the best-use conditions of pressure washing:

- Evaluate the efficiency of cleaning various materials (wood and metal plates, synthetic boat hulls, concrete walls, equipment) at different weathering states and pressure and temperature settings
- Compare solvents: efficiency related to cost, availability, dispersibility, and solubility in water
- Evaluate the efficiency of a specific protective product: Elf Filmogene, a powder made of alginates (seaweeds) that can be applied in the form of a gel on structures and that prevents oil from adhering on the surface

Experimental design

Test site. The trials were conducted on a Cedre trial zone in Brest. These facilities, located in the industrial and port area, are specially dedicated to oil spill response and have been used for training and experimentation for more than 10 years. The core of the facility is its 6000-m^2 lagoon and artificial sand beach, which includes several rock and pebble sections. A concrete slipway at the border of the beach allows for equipment and a nautical means of launching into water. Next to the lagoon is another deeper basin used as a water reserve for the lagoon (e.g., for tide simulation) or for equipment deployment. The facilities also include two warehouses for equipment storage and workshops as well as a building dedicated to offices and a conference room (Figure 1).

Initially containing brackish water, the lagoon was entirely emptied and refilled with new seawater prior to the trials to ensure a sufficient level of salinity for the bitumen buoyancy. The density of the water was measured at 1.021 during the trials.

Equipment tested. The main pieces of equipment and techniques tested during these trials were as follows:

- For recovery on water: Ro-Clean Desmi "Terminator" weir skimmer, Lamor "Mini" brush skimmer, Vikoma "Kebab" disc skimmer, Ro-Clean Desmi "ScanTrawl" net, and manual collection
- For recovery on sandy beach: Rolba screening machine, manual collection
- For cleanup of polluted substrates: Le Floch and Lamor pressure cleaners for hard surfaces (rocks, man-made structures), cement truck for pebbles cleanup, Jet Systems scrubbing machine for sand
- Cleaning agents used: Total Ketrul 210 solvent, Nalco/Exxon Corexit 9580, Marine Services Inc., Ori-Clean solvents, and diesel oil

Setup

Bitumen preparation. The bitumen was prepared in a separate tank next to the lagoon by pouring 1 m^3 of Orimulsion (corresponding to 700 liters of bitumen) in about 8 m^3 of seawater. From this Orimulsion dispersion, bitumen was produced by making bitumen droplets collide as a result of an extensive pumping action inside the tank (by a Desmi 210 screw pump) and a surface churning up (by a centrifugal pump), the combined action of which destabilized the Orimulsion in the form of a foam that rapidly collapsed into a thick layer of bitumen at the surface.

Bitumen application. On the sand beach, bitumen was applied in fine ribbons (approximately 5 mm thick, thanks to a small tank fitted with apertures) on a 1-m-wide area extending about 30 m. The pebble sections were coated the same way on a few square meters.

Materials plates were dipped into the preparation tank and were also heavily covered (thickness up to 10 mm). Bitumen was hand-applied on man-made structures such as a concrete wharf and a boat hull in layers of irregular thicknesses.

Lastly, the equipment chosen for the equipment cleanup test was the Desmi pump used to process the Orimulsion in the preparation tank; it was coated with a thick layer of weathered bitumen.

Recovery and cleanup tests. The trials lasted 4 days and took place on various locations in the trial zone. The Lamor skimmer and Ro-Clean trawl net were operated on the lagoon, whereas the Ro-Clean skimmer was operated in a separate tank. The screening machine was run on the

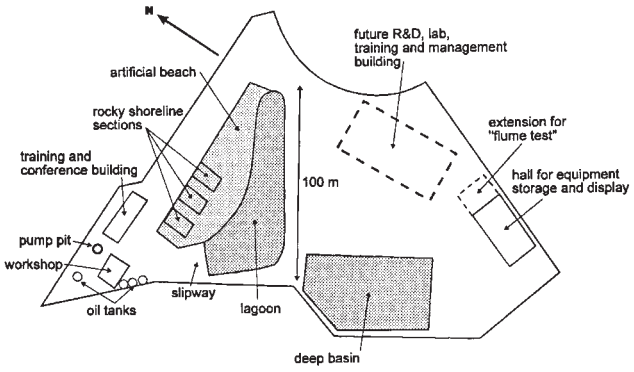

Figure 1. Cedre trial zone

artificial beach. Cleanup of structures and sediments was done on the slipway next to the lagoon.

Results

For the sake of clarity, the test results are gathered according to the different phases of oil spill response: first, recovery on water (skimmers, trawl net, manual collection); then selective recovery onshore where the slicks have grounded (screening machine, manual collection); and finally cleanup on shoreline (high-pressure cleaners for rocks and structures, cement trucks for pebbles, and scrubber machine for sand) and on equipment.

Recovery on water

"Terminator" weir skimmer

Principle. This is a weir skimmer with an embarked archimedian screw pump. The weir is self-adjustable thanks to a rubber lip adapter. The buoyancy of the system is ensured by three polyethylene floaters. The pump is a Desmi 250 vertical archimedian screw pump designed for viscous products.

Setup. The skimmer was floating in a 3.4 × 1.5 m tank filled up to 1 m with seawater and discharging into a separate tank. Bitumen was poured in large patches (about 200 liters).

Observations and conclusions

- Pickup ability of weir: poor in these test conditions, all bitumen having been manually forced into the weir. However, it is estimated that pickup ability would improve if the bitumen were in the form of small tar balls or weathered patches floating in open sea, as observed elsewhere (Gunter *et al*., 1995).
- Pump: successful in transferring bitumen in the form of lumps mixed with large quantities of water (with the Desmi 210 straight screw pump used for processing, the only one that managed to do so during the trials).
- Bitumen content of discharge fluid: low (around 3%) but not a major problem if discharge tanks are equipped with sufficient drain-off valves.

Brush "Mini" skimmer

Principle. Small oleophilic brush skimmer for dynamic and static use. Fitted for these trials with a Marflex pump for bitumen discharge.

Setup. The skimmer was used on bitumen film formed on the lagoon inside an approximately 10 × 5 m area limited by sorbent booms. Discharge was in a tank on the slipway.

Observations and conclusions

- Pickup ability of brushes: very good in the test conditions; brushes were rapidly covered with bitumen. However, difficulties were experienced with bitumen transfer from brushes to pump inlet.
- Transfer capacity of Marflex pump: looked poor; no bitumen was seen in discharge tank. Although known to be adequate on viscous oils, the Marflex pump has to be replaced for operation on bitumen (by Ro-Clean Desmi 250, for example).

Complementary tests are planned by Lamor after changing over to a Ro-Clean Desmi pump.

Trawl net

Principle. This net was a reduced version of the ScanTrawl net system manufactured by Ro-Clean Desmi and already blank-tested in 1996. With a 6-m width wing to wing, it was specially designed to be tested with bitumen. It consists of a fine-mesh net that is surface-trawled by two boats through the bitumen, which is collected and accumulated in a disposable codend (sock) at the back of the net. The two trawl entrance wings are maintained at the surface by polyethylene inflatable floaters.

Setup. The net was tested without its plastic bunt (sleeve) for a better observation of bitumen pickup. For maneuverability purposes, it was trawled by a single boat with the help of a 6-m metallic jib fixed across its stern and the two warps attached to each end of the jib. For better control of bitumen spill and facilitated observation, the boat was held in a fixed position with its bow against the wharf of the lagoon and the boat engine creating the flow of water through the net. A first try was made on bitumen lumps (fist-size) thrown from the boat into the net entrance. A second try was made by letting a large patch be picked up by the net.

Observations and conclusions

- The ScanTrawl net was able to pick up weathered lumps of bitumen and accumulate them in the disposable codend.
- It did not look suitable for large patches of fresh bitumen, which tend to gum the net entrance. Indeed, because of the design of the wing, there is a risk of trapping patches between the mesh and the floater. This problem has been discussed with the manufacturer, and it is believed that it can be easily remedied.
- Bitumen flow through the net showed that a smaller mesh size would be more appropriate. However, increased drag forces due to smaller mesh should be carefully assessed because they can lead to net overflow if the operating speed is not reduced.

Manual recovery on water

Principle. Weathered patches or film of bitumen are manually removed from the water edge with the help of tools (pitchforks, squeegees, rakes, brushes) or directly by gloved hand.

Setup. A proper test was not specially implemented for this technique. However, it appeared to be a swift and successful means of recovering the bitumen film at the lagoon surface after the various skimmer tries.

Observations and conclusions

- This technique is the only one that can be implemented in water where skimmers cannot operate (i.e., in very shallow water or in poorly accessible sites).
- When the bitumen is cohesive, this method can be very efficient and can even compete with skimmers or a trawl net near the shore where the water level allows it.

Recovery on sand

Sand-screening machine

Principle. The screening machine is currently used for tourist beach cleanup and is powered by an agricultural tractor. The system includes a vibrating front blade that takes sand out to a perforated conveyor belt, which screens the sand and carries the remaining debris to a waste bucket. It works best on solid debris or on very viscous and weathered products, hence its expected suitability for bitumen.

Setup. Bitumen was spilled on the beach in the form of ribbons and tar balls and left to weather for 24 hours to simulate a bitumen slick that was being deposited by the tide on the sand and that weathered as the tide went down. The Rolba screening machine was connected to the power takeoff of the Cedre tractor.

Observations and conclusions

- The screening machine was fast and efficient in collecting weathered bitumen deposited on sand, either in the form of tar balls or as thin plates.
- The operating speed can be fine-tuned to obtain a very high bitumen content in the wastes. Blade depth can also be adjusted for a better speed/efficiency compromise, although it was not done during these trials.
- This technique should be implemented on wide beaches that give easy access to agricultural machines and on which bitumen and sand can dry between tides.

Manual collection on sand

Principle. Weathered patches or balls of bitumen are manually removed on sand with the help of tools (pitchforks, squeegees, rakes, brushes) or directly by gloved hand.

Setup. This test was made on the bitumen laid for the screening machine test and left on purpose on an 0.8 × 2.0 m area. Shovels, forks, and a waste bucket were the tools used.

Observations. Most of the bitumen could be easily gathered in heaps with the tools. Smaller lumps passed through the forks' teeth, and tools like rakes would have been useful at this stage. Remaining small lumps were eventually collected with gloved hands in a more tedious operation.

Observations and conclusions

- Manual collection using tools or even bare hands is possible and does work on weathered bitumen deposited on sand.

- Large patches and plates are easy to pick up using hand-held tools, and in this case manual recovery may be preferable to mechanical screening.
- Small lumps that get through forks and rakes can be very tedious to collect, and manual collection should be implemented on sites where mechanical screening is not possible (difficult access, presence of boulders or rocks, wet sand)
- Improved collection tools can be considered (fine rakes, metallic mesh associated with forks, etc.).

Beach Cleanup

Pressure Cleaners

Principle. After the raw removal of bitumen (collecting, scraping, sucking up), beach cleanup consists of washing the polluted surfaces with cold or hot water at high pressure. A power pack generates high-pressure (and possible high-temperature) water, which is discharged through a flat nozzle. Cleanup products are strongly recommended with viscous and weathered products such as bitumen and were therefore used during these trials.

Setup. High-pressure cleaners were evaluated on rocks, wood and metal plates, the boat hull, and the concrete wharf, the last of which was partially covered with Elf "Filmogene" preventive product. Le Floch high-pressure hot water cleaners were set at their maximum capacity—140 bars and 100°C at the nozzle—whereas Lamor high-pressure cold water cleaners operated at about 200 bars.

On rocks, bitumen was left to weather for 3 days. An initial cleanup took place without solvent. Then Corexit 9580 was applied on what remained from the first raw cleanup; it was allowed to soak for 15 minutes, and another cleanup was then performed.

Two 1-m^2 wood and steel plates were covered with thick, fresh bitumen, and both were cleaned the same way: half of a plate was first cleaned without solvent, and then Corexit 9580 was generously sprayed all over the plate and left to soak for 10 to 15 minutes. The remaining bitumen and the solvent half was cleaned, and finally the first half (solvent on bitumen marks) was cleaned again.

On both sides of a small boat, fresh bitumen was applied on the hull and Corexit 9580 sprayed on half of each side. Then a pressure wash was performed: one side was washed with a Le Floch high-pressure hot water cleaner, and the other one with a Lamor high-pressure cold water cleaner.

Observations and conclusions

- Bitumen can be removed using pressure cleaners and solvents, even if the operation is moderately tedious. The cleanup is facilitated if the bitumen thickness is reduced as much as possible so that solvents can better soak into the bitumen and perform their action. However, this necessitates taking excess bitumen out, which represents additional effort and time.
- Scraping using tools such as knives or trowels is extremely laborious and difficult to envisage for large-scale operations; instead, air conveyor systems that suck bitumen up could advantageously replace scraping.
- Cleanup with high-pressure cold water (Lamor cleaner) is less efficient than with hot water at lower pressure (Le Floch cleaner).
- Solvents seemed to have comparable efficiency, and if the goal is to recover the effluents on water, the most suitable solvents are petroleum cuts (because they do not disperse), preferably with a low aromatic content (because they are less toxic), such as Total Ketrul 210.
- The use of high-pressure cleaners to remove bitumen from tools or equipment should be reserved for large pieces of equipment; others can be left to soak in a diesel tank before being flushed clean.

Filmogene protective product

Principle. This product is currently being developed by Elf Aquitaine and is at present not commercially available. It is made of alginates (seaweeds) and is a powder that, mixed up with water, yields a gel-like product that can be sprayed onto fixed structures (wharf concrete walls, stony shoreline, metallic structures) or mobile equipment (boats, skimmers, booms) in a preventive way prior to contact with the hydrocarbon pollutant. After a short drying time (3 hours is recommended), it builds up a thin layer or film (hence the name) on the treated surface. Hydrocarbons do not adhere to this surface and tend to slip off without causing contamination.

Setup. The test was carried out on the concrete wharf of the lagoon. The product was sprayed on a 1-m^2 wet area and left to dry for 2 hours (good weather conditions accelerated drying). Another 1-m^2 area was wetted and bitumen applied on both sections.

Observations and conclusions

- The efficiency of the Elf Filmogene product on concrete had already been tested by Cedre with medium-viscosity oil, and it was confirmed here on the bitumen: cleanup time was reduced by a factor of 2 and the final state of the concrete was better when Elf Filmogene was used.
- Considering the difficulty of cleaning up surfaces contaminated by bitumen, the preventive action of this Filmogene product should be kept in mind.

Cement mixer for pebble cleanup

Principle. This operation consists of physically removing sediments from beach and putting them back in place after washing them in a nearby station. The washup station can be a specially designed washup machine, washup equipment for quarry sediments, or, more simply, cement mixing trucks. This last option was implemented.

Setup. About 150 liters of pebbles contaminated with 40 liters of bitumen were fed into the cement mixer. Three runs were made with the Corexit 9580, diesel, and Ketrul 210 cleaning agent (Ori-Clean solvent had been found to disperse too much to be recovered on water). Each time 20 liters of solvent were added (1:2 solvent-to-bitumen ratio). The pebbles were left for 10 minutes mixing with solvent, and then another 10 minutes in solvent added to water, and finally left 5 minutes to settle. Effluents and pebbles were discharged on the slipway, where flushing was carried out using a fire-fighting type of water hose.

Observations and conclusions

- This process was successful in removing most of the bitumen from heavily contaminated pebbles. Efficiency can be improved on actual work sites through better flushing (grids or skips systems) and recirculation of effluents in the mixer.
- Nondispersing products should be chosen as solvents; these settle in the cement mixer better, and effluents can be better recovered on water. Petroleum cuts such as simple diesel oil or Total Ketrul 210 can be used.

Sand scrubber

Principle. This transportable unit cleans sediments through the scrubbing and leaching action of its jet pumps. Contaminated sediments are fed through a hopper into a mixing chamber, where jet pumps create a fast stream of fluid emitted from a nozzle to fluid surrounding the jet; this causes vigorous rubbing of particles against each other. Gravity separates the clean sand, oil, and water, and the water is recirculated into the system.

Setup. The scrubber unit was set up near the lagoon. Contaminated sand was prepared by mixing 40 liters of bitumen and 200 liters of sand in the cement mixer. Some lumps of bitumen remained within the sand after the mixing. The sand was manually fed into the mixing chamber of the scrubber and recirculated two more times in the system.

Observations and conclusions

- The first discharged sand incorporated bitumen particles coming from the lumps shattered by the jet pumps. However, after two recirculations in the system, the sand came out satisfactorily clean. Cedre lab tests indicated that a hydrocarbon content of 6% in the polluted sand fell to 0.046% after the last washup (percentages related to dry sand). The scrubber showed good potential for cleaning Orimulsion-contaminated sand, even if problems were encountered during the trials, probably because of the design of the demonstration model.
- This process can be a way of cleaning sites on which selective recovery is not possible (contamination with fresh Orimulsion or fine bitumen particles).

Conclusions

These tests proved that solutions exist or can be found to cope with pollution by Orimulsion bitumen, even if many pieces of equipment and techniques commonly used to deal with "usual" hydrocarbon pollution events are inefficient. Considering the various aspects of bitumen, a single recovery or cleanup device cannot be recommended to the exclusion of all others; instead, the trials have highlighted different options that can be taken depending on shoreline configuration and bitumen state.

Recovery on water. In the test conditions (cohesive floating bitumen), the skimmers tested did not prove effective, and manufacturers are working to improve their design for bitumen. However, in different tests under different conditions, other skimmers and recovery equipment have been reported to be successful on bitumen recovery (Gunter *et al.*, 1995; Middleton, 1995). Trawl nets such as the Ro-Clean Desmi Scan-Trawl system are to date the best way of collecting floating weathered bitumen. To reduce the risk of trapping bitumen between the net and the floater, design changes were proposed: the mesh part of the wing should be sewn at the bottom of the floater, and the manufacturer suggested a possible 3.5-mm^2 mesh in place of the present 5-mm^2 mesh to limit bitumen flow through the mesh.

It should also be noted that manual recovery can be successfully implemented near the shore by using tools (pitchforks, squeegees, rakes, brushes) or directly by gloved hand.

Shoreline cleanup. If bitumen comes ashore, the solutions will depend on the shoreline substrate and the bitumen state.

Mechanical screening of sandy beaches proved efficient and should be implemented when conditions allow it: with weathered bitumen, dry sand, and wide accessible beaches.

Manual collection can also be efficient on large weathered bitumen patches deposited on sand.

Pressure washing with solvents can remove bitumen from hard surfaces such as rocks, structures, and equipment. Taking out excess bitumen is strongly recommended prior to solvent spraying: air conveyor systems can be proposed, and scraping can be used as fallback.

Pebbles can be cleaned by removing the sediments from the beach, cleaning them in a cement mixer or in a dedicated cleaning machine with a solvent, and putting them back in place.

The types of solvents recommended are petroleum cuts with low aromatic content (e.g., Total Ketrul 210).

Because of the difficulty of cleaning bitumen, preventive action is recommended, such as the use of nets and the Elf Filmogene product (not yet commercially available).

Cleanup of equipment. The use of solvents and high-pressure cleaners to remove bitumen from tools or equipment should be reserved for large pieces of equipment; others can be left to soak in a diesel tank before being flushed clean.

Again, Filmogene product can be sprayed as a preventive measure on equipment and tools before they are used in Orimulsion/bitumen.

Further work. Further work could include the study of bitumen behavior and fate, further skimmer tests (still to be investigated is the transfer of bitumen from a pickup device, such as a brush, to a pump inlet), trials of air conveyor systems to suck up excess bitumen from rocks or structures, and improving the tool design for manual recovery when bitumen is in the form of small lumps.

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