ENVIRONMENTAL IMPACTS OF OIL SHALE AND POLLUTION CONTROL TECHNOLOGIES

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Summary

Environmental impacts of oil shale industry mainly include the wastewater discharge, air pollution, and shale ash disposal.

Wastewater discharged from a retorting plant contains oil, suspension solid, and oxygen, nitrogen, and sulfur-compounds; it can be treated by sedimentation, oil interception, flocculation, air floatation, and biological treatment.

Air pollution is mainly due to the fly ash, sulfur dioxide, and nitrogen oxides contained in the flue gas leaving the chimney of the oil shale boilers in the power plant. High efficiency dust remover, high efficiency sulfur dioxide absorber or adsorber should be used, and adequate technology should be applied for low emission of nitrogen oxides.

Shale ash formed from an oil shale power plant and oil shale retorting plant may be used for mine backfilling, for agricultural utilization and cement making.

Environmental impact is one of the main factors influencing the development of the oil shale industry. Many countries have paid much attention and developed different effective pollution control technologies.

1. Introduction

The oil shale industry, including oil shale mining, crushing, sieving, retorting, combustion, and oil upgrading, will cause environmental pollution, such as: wastewater from mining, retorting, upgrading, ash moisturing, etc.; dust produced from mining, crushing, sieving, retorting, and combustion; oil sludge, shale ash and retorted shale handling, and disposal; waste gas from retorting and combustion; as well as land disruption due to surface mining.

In the developing oil shale industry, the oil shale companies, with the support of governmental agencies, and the cooperation of research institutes and related universities, have made an investigation of the environmental problems. Over several decades, many pollution control technologies have been developed in order to meet the pollution control regulations, especially to meet the waste disposal limitations. Sometimes, the waste disposals or impurities are converted to valuable products, such as the shale ash used for making cement, and the wastewater extracted for producing phenols.

2. Wastewater Composition and its Treatment

The quantity of wastewater from oil shale retorting is largely dependent on the moisture content of oil shale feed and the retorting condensation and recovery system. For example, Chinese Maoming oil shale, in the rainy season, contains more than 15% moisture; furthermore, in Fushun and Maoming, the hot vapor-gas mixtures coming from the retorts are cooled and condensed by direct water scrubbing, thus resulting in a large amount of added water. Part of the water has to discharge as wastewater; it is reported that, for 1 ton of shale oil produced, 9 tons of fresh water is consumed and 5 tons of wastewater, which contain oily material, phenols, pyridines, sulfides, and dusts, has to be discharged.

In other cases, such as in the Estonian Kiviter Process, and Brazilian Petrosix Process, where the vapor-gas mixture leaving the retort is cooled by indirect water cooling and the oil shale contains little water, then the excess water is only the pyrolysis water produced from oil shale pyrolysis. This usually amounts to a large percentage of the oil shale fed, and may be used for moisturing shale ash for disposal. The pyrolysis water, after being separated from the shale oil, is cooled in a cooling tower and recirculated for indirect cooling of vapor-gas mixture. Such a scheme creates zero discharge of wastewater.

The composition of discharged water varies with different kinds of oil shale. In Estonia and Russia, due to the high content of oxygen in kukersite oil shale, phenols and resorcins are dissloved in condensed water and can be recovered. In Fushun and Maoming, ammonia and pyridines are contained in exit vapor-gas mixture, the ammonia is absorbed by dilute sulfuric acid; however, due to the dilution of the condensing vapor (from retort) by direct cooling water, the concentration of pyridines is too low for recovery.

2.1 Wastewater Treatment in the Chinese Maoming Oil Shale Company

Wastewater treatment technology was developed at the end of 1980s, by the Chinese Maoming Oil Shale Company; the technology developed is similar to that used in conventional crude oil refinery, but is modified for treating shale oil wastewater with higher contents of impurities. Retorting water is first treated by static sedimentation, oil interception, flocculation, air floatation; then undergoes biological treatment in a towered biological filtration pond. The chemical oxygen demand (COD), biological oxygen demand (BOD), volatile phenols, and hydrocarbon contents can be greatly reduced and the wastewater discharge can meet the environmental regulation.

The treatment data are shown in Table 1. The treatment cost is reported not to be higher than that of the conventional refinery.

	COD (mg/L)	**BOD (mg/L)**	**Oil (mg/L)**	**Phenols (mg/L)**	**Suspension (mg/L)**
Wastewater	29 000		2660	230	2300
Settling (200 h)	24 700		960	210	720
Interception and flocculation	22 000		630	130	470
Air floatation	10 300		170	60	260
Water dilution	1900	580	60	20	—
Biological treatment	900	52	20	1	—

Table 1. Wastewater treatment data

2.2 Oil Sludge Treatment

A certain amount of shale fines is entrained in the retort of vapor-gas mixture. A kind of mud-like oil sludge composed of heavy shale oil, water and shale dust is formed in spray washing of off-gas, as the first step of the cooling and condensation system. Oil sludge along with the washing oil is collected and separated in settle tank, The composition of oil sludge varies greatly with the retorting processes, and spray washing conditions. Composition of oil sludge from retorting plant in Chinese Fushun Refinery is shown in Table 2.

Discharge temperature (°C)	**Oil (wt%)**	**Water (wt%)**	**Fine Residue (wt%)**	**Specific Gravity $4^{o}C$ /$4^{o}C$**
70–80	28–34	15–30	40–50	1.2–1.2

Table 2. Oil sludge composition

The amount of oil sludge is about 2% of shale oil produced; its formation causes not only the loss of shale oil but also pollution of environment.

Centrifuge drying has been used in the Fushun Refinery to reduce the water content in oil sludge to below 10%, the dry mass after centrifuging was charged back to the retort, thus eliminating a source of pollution. The recharged dry mass amounts to ~10 m^3 each retort per day, and accounted for only 8% of the shale charge, causing no adverse effect on the operation.

2.3 Wastewater Treatment Plant, in Kohtla Jarve, Estonia

The wastewater treatment plant at the Kiviter Oil Shale Chemicals Company in Kohtla-Jarve, Estonia, is a two-stage biological treatment system. It treats oil shale industrial wastewater and sewage not only from Kiviter, but also from other nearby industries and municipalities. This treatment plant treats between 28 000 and 30 000 tons per day of wastewaters, and will increase to 55 000 tons daily. The municipal wastewaters are pretreated in the plant, which provides comminuting devices, vortex grit removals systems, and primary solids sedimentation. The industrial wastewaters mixed with the pretreated municipal wastewaters enter into aerated equalization basins, for two-stage activated sludge sedimentation. Treated effluents are discharged via a pipeline and deep-water outlet to the Gulf of Finland. Table 3 presents the data of treatment.

	Wastewater In	**First stage**	**Second stage**
BOD (Tot., mg/L, 7 days)	114–292	69–255	19–62
BOD after settling (mg/L, 7 days)	—	34–173	10–29
Phenols, volatile (mg/L)	5–10	0.3–5.0	0.05–0.25
Phenols (Tot., mg/L)	16–34	6.6–23	2.3–7.6

Table 3. Two stage biological treatment data of wastewater in Kohtla Jarve

Oil shale enterprises and research institutes are continuing to make efforts to meet the regulations required by Estonian Government.

3. Air Pollution due to the Emissions from Oil Shale Plant

The behavior of oil shale in the combustion process and the emissions of environmental pollutants have been studied for many years.

3.1 Emissions from Oil Shale Power Plants in Estonia

Estonian power production is almost entirely based on oil shale combustion. Two big power plants with the combustion of pulverized oil shale are in operation near Narva: the Estonian Power Plant (1 600 000 kW) and the Baltic Power Plant (1 400 000 kW), and two small ones in Kohtla Jarve (39 000 kW) and Ahtme (20 000 kW). At its peak, in the 1980s, about 25 million tons of oil shale were burnt in power plants every year. In 1998, about 13 million tons of oil shale were burnt. However, the impact of oil shale combustion to the atmosphere is still serious. Estonian oil shale is specific low-grade fossil fuel, in comparison with coal; the oil shale is rich in sulfur and mineral matter, with high content of carbonates. During combustion, with the dissociation of carbonates (Ca and Mg), essential desulfurization of flue gas by ash sulfation in boilers and gas ducts takes place. The rates of sulfur capture, range from 40% to 90%, under different conditions, have been reported. However, the sulfur dioxide remaining in flue gas is still excessive, thus forming the great pollution problem. Although the plant has been equipped with electrostatic precipitators and bag filters, the fly ash concentration in flue gas is still high. Table 4 shows the concentration ranges of the pollutants in flue gas of the two Narva Power Plants.

All the particle concentrations measured in both power plants (1440–6250 mg/Nm^3) are remarkably higher than the German emission standard (40 mg/Nm^3) permits. It is due to the insufficient capacity of electroprecipitators. The dust particle amounts to about 1% of the oil shale burnt. At the end of the 1990s, a new electroprecipitator was installed into one 400 MW block in the Estonia Power Plant, the emission from this block is below 100 mg/m^3.

Power plant	**Estonian**	**Baltic**	**Baltic**
Boiler type	TP-101	TP-17	TP-67
Sulfur dioxide	770–2280	640–3300	1340–2570
Nitrogen oxides(as nitrogen dioxide)	130–220	160–210	190–250
Hydrogen chloride	6–46	14–40	40–57
Polyaromatic hydrocarbons	0.1–3.2	—	0.04–0.12
Dust particle	1400–6250	1730–3320	1440–2900

Table 4. The concentration ranges of the pollutants in flue gas of the two Narva power plants (mg/Nm^3)

The sulfur dioxide concentration in flue gases remains very high (e.g., 640–3300 mg/Nm^3) above the limit of the German emission standard (300 mg/Nm^3). Nitrogen oxide emissions of Estonian oil shale combustion are much lower than that measured in conventional coal-fired power plants. The highest concentration is 250 mg/Nm^3, which is *below* the German emission standard (590 mg/Nm^3).

Besides, the concentrations of hydrogen chloride, polyaromatic hydrocarbons, and hydrogen fluoride, carbon monoxide, and total hydrocarbons are all below the German emission limits. Again, the particulate heavy metal concentrations (Pb, Cd, Zn, Cu, Ni, Cr, Co, As, Hg, Mn, Mo, Se, and Tl) have also been measured; the total concentrations exceed the German emission standard, due to the low efficiency of the particle control devices. Table 5 shows the yearly emissions of pollutants from the Narva Power Plants, the emission decrease in recent years is mainly due to the reduced combustion capacity. Table 6 shows the emission of shale oil plants, tons per year

	Estonian Power Plant			**Baltic Power Plant**		
	1992	1994	1998	1992	1994	1998
Sulfur dioxide	60 400	48 300	—	78 000	49 600	—
Nitrogen oxide	6900	5300	—	7000	4900	—
Dust particle	112 300	91 000	33 000	74 000	49 600	29 500

Table 5. Yearly emissions of the Narva power plants (tons/year)

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Biographical Sketch

Jian Qiu Wan is a Professor of Education; she graduated from the University of Petroleum, (former Beijing Petroleum Institute), majoring in Synfuel, in 1956. She has published over 50 research papers published in international and domestic journals, and has attended meetings in the field of processing of oil shale, coal, petroleum, as well as the plastic waste to fuels and chemicals. Professor Jian is co-author of four books. She teaches graduate courses on: oil shale processing, petroleum formation kinetics, etc. Awards granted: six awards by ministries. International activities: visited US, Canada, Japan, and Thailand for scientific exchange and conferences.