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Review

Industrial extraction pilot plant for stripping H_2S gas from Black Sea water

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ABSTRACT

The results from the laboratory-scale extraction pilot plant unit for the separation of H_2S from Black Sea water lead us to build a novel industrial extraction pilot plant to concentrate H_2S from 10 ppm to above 10000 ppm. The processing of 10^9 m^3 of water containing 10 ppm will produce 0.833 tons of hydrogen and therefore a technology for extraction and concentration of H_2S is essential.

The conceptual pilot plant proposed in this paper is in principle similar to the laboratory pilot plant developed in the University of Duhok, Iraq, and it could work to pump water directly from Black Sea. It contains a screen with electrical heater to fix the temperature of stripping, a water chiller at the top to separate any water droplet or vapor. The research on industrial pilot plant has shown that, this unit could operate both on and underneath the surface of the sea.

1. Introduction

Hydrogen sulfide gas is flammable and poisonous. It is soluble in water, and it can also corrode pumping metals such as iron, steel, copper and brass. The equilibrium concentration of H_2S gas in the Black Sea is 10 ppm at 1000 m depth. H_2S should be extracted without conversion to other molecules and it should be concentrated to 10,000 ppm or above, in order to bring it to the similar concentrations in natural gas for which the technology has been well developed to produce hydrogen fuel. The solution of H_2S gas in water is non-ideal and the extraction of this gas from water should be through Henry's law and it depends on the physical and chemical variables (concentration, pH, salinity, pressure of stripping pump, temperature, height of the stripping tower etc.). These variables can be studied through Le Chatelier's principle to find the equilibrium concentrations of H_2S in Black Sea.

The daily production of H_2S by sulfur reducing bacteria (SRB) is about 10,000 tons in the Black Sea and the reservoir of H_2S is estimated to be 4.587 billion tons [1]. The mixture of H_2S in water is considered as a non-ideal (gas–liquid) solution. Both molecules can produce hydrogen but H_2S is much easier to dissociate than water due to the bonding structure of the molecules [2].

1.1. *Survey for concentration of H_2S at different depths of the Black Sea*

Literature survey for distribution of H_2S and oxygen in the Black Sea shows different concentrations of H_2S at different

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Nomenclature

AGE	acid gas enrichment
BTU	British Thermal Unit
CH_4	methane gas
CS_2	carbon disulfide
CP	Claus process
FH	feed heat
H_2S	hydrogen sulfide
HT	heat transfer
HSMR	hydrogen sulfur methane reformation
IGT	Institute of Gas Technology
kJ	kilo joule (kJ)
kWh	kilo watt hour
MCTGC	modified Claus tail gas cleanup
NG	natural gas
LH2	liquid hydrogen
ppm	parts per million (ppm)
PV	photovoltaic
PEP	photoelectric power
SAC	superadiabatic combustion
SMR	steam methane reforming
TGCU	tail gas clean unit
ΔH	heat of reaction

depths of the sea, ranging from 7 to 14 ppm, Fig. 1 has been treated statistically and shows that at the bottom of the sea at 2200 m H_2S concentration is about 14 ppm, which is due to the formation of this gas from sulfur and $SO_4^{=}$ ions by anaerobic bacteria (sulfur reducing bacteria), while at the surface the concentration of H_2S is zero down to the depth of about 100 m due to the action of sulfur oxidizing bacteria (SOB) Fig. 1 [3].

Some of these reports have been using different units for the concentration of H_2S, which give conflicting results. In this paper only SI units will be employed for all the physical and chemical variables. The concentration of oxygen is about 8–9 ppm at the surface of the Black Sea and it declines to zero at about 100 m depth due to the activities of sulfur oxidizing bacteria on the surface of the sea which oxidize H_2S to sulfate. Therefore the concentration of H_2S is zero at the surface and it starts growing at the depth of 100 m. There is a natural equilibrium between these two types of bacteria at the bottom and surface of Black Sea. Fig. 1 shows that Le Chatelier's Principle is applicable to all these reactions at the depth of 1000 m. Bio activities of both SRB at the bottom and SOB at the surface and at different depths and the activities of photosynthesis bacteria in Black Sea shown in Fig. 1 will explain the dissociation constants K_1 and K_2 of H_2S with its ions HS^- and $S^=$ at salinity and pH of Black Sea water. In the natural equilibrium zone in Fig. 2 the concentration of H_2S is 10 ppm at 1000 m depth, where the temperature is 8 °C and the salinity is 20,000 ppm.

Fig. 2 shows the concentrations of H_2S and oxygen as a function of depth of water from different researches [6,7]. Le Chatelier's principle can be summarized as:

If a chemical system at equilibrium experiences a change in concentration, temperature, or total pressure, the equilibrium will shift in order to minimize that change [4].

According to Le Chatelier's principle for chemical equilibrium the characteristic of H_2S in the Black Sea at equilibrium depth will not be affected when this gas is pumped to the surface of the sea and that was the reason why this depth was chosen.

1.2. *Natural equilibrium in the Black Sea*

Black Sea is well known to be rich in H_2S gas. Large amounts of H_2S are formed by SRB bacteria in the sulfur deposit at the bottom or from organic matter accumulation of larger rivers pouring into the Black Sea and it may be due to the fractures and mud volcanoes, as well as the destroyed gas-hydrate deposits, which are transformed by these SRB bacteria into H_2S gas. Fig. 2 shows this picture.

Surveys on the concentration of H_2S in Black Sea have been treated statistically and show that the concentration is zero at the surface, and it increases gradually after 100 m, then it will reach 10 ppm at 1000 m depth and 14 ppm at the bottom of the sea (Figs. 1 and 2).

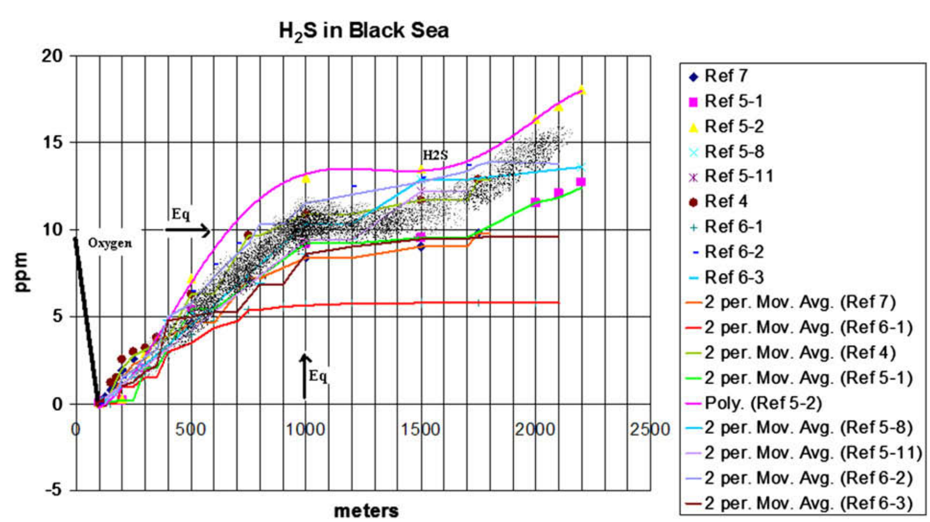

Fig. 1 – Concentration of H_2S and O_2 in Black Sea water from different authors.