DOE/EE/15626--T6

Final Technical Report Relating to Grant Number DE-FG01-95EE15626

"Prototype Development of an Apparatus to Locate and Map
Sea Floor Petroleum Seepages"

Awarded to K. F. Thompson, Petrosurveys, Inc., Dallas, TX.

ABSTRACT

The objective of the grant was to design, build, and test two autonomous instruments to measure vertical profiles of electrical potential in sea floor sediments. The objectives were fully met when the instruments were successfully deployed in 1800 feet of water at known petroleum seepage sites in the Gulf of Mexico. The instruments were proven to be able to measure and record signals known to be appropriate to sediments altered by seepage. Two known seepage sites were visited on September 18th and 20th, 1996. At the first, a small-scale instrument capable of measuring 60 cm into the sediment was repeatedly emplaced by the manipulator arm of a research submarine, along a sea floor traverse. Further, the large-scale instrument, having a probe 3.3 m in length, was deployed by steel cable from the ship and emplaced in the sediment under gravity. Both successfully recorded data from multiple electrodes, revealing the expected negative potentials (Eh values as low as -230 mV) at, and close to, the sediment-water interface, instead of at the normal depths of 3 to 4 m.

BACKGROUND

Two remotely-operable multi-electrode electrometer systems were designed and built to the specifications of Petrosurveys, Inc., by the Department of Engineering, Harbor Branch Oceanographic Institution. Precursor models were successfully tested in near-shore waters in March and May, 1996.

On September 9th, 1996, the Research Vessel Edwin Link, 168 feet in length, operated by Harbor Branch Oceanographic Institution (HBOI), departed Fort Pierce, Florida, for a seven day scientific investigation of petroleum seepage sites in the Gulf of Mexico. Half a day of ship's working time was provided by the above grant, and a further half was donated by the Engineering Department, HBOI, for the purpose of testing the subject instruments. The cruise was commissioned by the Chief Scientist, Dr. H. Roberts, of the Coastal Studies Institute, Louisiana State University, whose interest centers on methane hydrate accumulations at seepages. As Co-Chief Scientist, my objective was the deployment and testing of the two devices built under the Grant for the purpose of measuring electrical potential in sea floor sediments.

The devices referenced above are basically identical in their electronics, differing only in size, and mode of deployment. Both comprise an elongate, electrically-insulated, cylinder bearing platinum electrodes, mounted below a pressure vessel containing an electrometer system, analog-to-digital converter, microcomputer, and power supply. The electrode voltages are scanned continuously at

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three second intervals from the time of deployment until recovery, when data are downloaded to a computer. In future, digital communication with the ship in real time will be incorporated. The systems are self-contained, capable of operating in an unattended mode on the sea floor to depths of 4000 ft. (1219 m). The larger system can be reconfigured to operate to depths of 9000 ft., or to 18000 ft without acoustic auxiliary systems.

RESULTS

Four deployment sequences were carried out. The first was of the 60 cm probe, at a well-investigated seepage known as "Bush Hill", in the protraction area Green Canyon Block 185 during a dive of the research submersible Johnson Sea Link II (Dive 2785) to a depth of 1800 feet. These observation sites are designated below as A to G, Deployment 1. The second through fourth deployments were of the 3.3 m device. The latter has an in-air weight of 1600 lbs., and was lowered by winch and 9/16 in. cable from the ship. It was tested at sites previously examined by the 60 cm system, at others adjacent, and at a gas-charged sediment (seepage) site previously defined by seismic exploration means in Mississippi Canyon Block 664.

All of the deployments yielded reproducible data of a nature known to be indicative of seepage-affected sediments. The latter aspect was verified during Dive 2785 in GC-185 where four sediment samples comprising 1 m-length cores were collected at certain of the Eh measurement sites. When recovered to the ship the sediments released visible trains of gas bubbles, possessed an odor of either hydrogen sulfide (known to accompany reducing conditions) or petroleum, and exhibited electrical potentials of -200 mV upon inserting the 4 in. probe of a laboratory Eh meter (Hach Co. Model EC10). Potentials are customarily expressed on a standard scale of Eh: voltage, or electrical potential, E, as it would have been measured against a standard hydrogen reference electrode, whence "Eh". Both the Hach EC10 and the probes employ a silver-silver chloride reference electrode which generates an electromotive force differing by 200 mV from that of a hydrogen electrode. Meter and probe system readings have been converted to standard values of Eh by the addition of 200 mV to the observations. Potentials measured with the EC10 were essentially equal to, or satisfactorily close to, those observed remotely at the sea floor with the probe systems.

The deployments revealed an unexpected attribute of the clays of the sea floor of the Gulf due to their richness in the clay mineral montmorillonite. This renders them exceptionally water-rich, plastic, and adhesive. Thus, when the probes were inserted into the sediment and withdrawn, a layer of clay up to 1.3 cm in thickness, adhered firmly. The platinum electrodes are flush with the cylindrical probe surface and data tended to be unchanged upon withdrawal of the probe at a given site until driven into the sediment at the next site. This showed that the observed signals originate within a layer no thicker than that adhering. Eh is therefore a very local phenomenon. Sudden changes of the recorded data from site to site, shown in the figures below, reveal that adhesion was not a serious shortcoming. Removal of the mud layer required energetic washing upon recovery and was carried out at the ship between drops at Sites 1, 2, and 3 in Deployment 4. No major gain over previous deployments was observed.

Deployment 2 was attempted using the constant chloride ion concentration of sea water as a reference medium for the reference electrode, instead of the usual 4 molar solution of potassium

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chloride. The latter is difficult to dispense. However, the reference electrode became discolored and this line of investigation was discontinued. The electrode was polished and its enclosure refilled with potassium chloride solution. In reporting the data of Deployment 2, experiment indicated the need to add a further 60 mV to the observations.

It was also found, as indicated in the literature, that chemical systems of limited poise (possessing low concentrations of species active in oxidation/reduction reactions) are prone to exhibit unstable, drifting signals. In nature, this is evident in oxidizing environments such as sea water. Deployment 4 illustrates the phenomenon. This data defect does not detract from the stable, well defined, observations of values of -185 to -230 mV observed with all electrodes at depths greater than 1.65 m. Drifting values between sites are of no consequence.

DATA

Locations of measurement sites are given in Table 1, and illustrated in Figures 1 and 2.

Table 1. Deployment Locations of Eh Probe Systems

System	Site	Latitude Deg., Min.	Longitude Deg., Min.	Protraction Block	Water Depth (ft.)
60 cm	A	27 46.95	91 30.46	GC-185	1801
60 cm	B	27 47.00	91 30.45	GC-185	1820
60 cm	C	27 47.07	91 30.45	GC-185	1881
60 cm	D	27 47.13	91 30.46	GC-185	1883
60 cm	E	27 47.19	91 30.46	GC-185	1873
60 cm	F	27 47.29	91 30.45	GC-185	1889
60 cm	G	27 47.43	91 30.41	GC-185	1854
3.3 m	C*	27 47.08	91 30.47	GC-185	1844
3.3 m	D*	27 47.14	91 30.45	GC-185	1837
3.3 m	E*	27 47.16	91 30.44	GC-185	1854
3.3 m	8	27 47.06	91 30.28	GC-185	1818
3.3 m	10	27 47.05	91 30.13	GC-185	1893
3.3 m	1	28 17.83	89 47.08	MC-664	1643
3.3 m	2	28 17.32	89 46.28	MC-664	1634
3.3 m	3	28 16.76	89 45.45	MC-664	1933

C*, D*, and E* are locations at which it was attempted to deploy the 3.3 m system at sites previously measured by the 60 cm system. Locations differ in position by 13 to 64 m on the sea floor, determined by Trackpoint II and GPS navigation equipment.

Figure 1

Table 2 presents Eh measurements observed immediately before the removal of probes from the sediment at each site, taken from the data files represented in Figures 3 to 6. All sites measured with the 3.3 m system exhibited strongly negative voltages at, and deeper than, the 1.65 m level. No information beyond that provided by the 1.65 and 3.15 m electrodes was provided by the 2.15 and 2.65 m electrodes, therefore the latter are not reported.

Figure 2

Complete data records (Figures 3 to 6) to illustrate the decisive fashion with which the apparatus records the expectable negative potentials in seep-affected sediments. Figures 3 to 6 present the greater part of the potential measurements made with the two systems. The records therefore mainly represent observations made during traverses between sediment insertion sites. The close similarity of the lift out values (upon withdrawal from the sediment) to the traverse values reveals the "memory" effect of the adhering film of mud. It will be noted that the uppermost electrodes in both systems (20 cm in the small system, 0.65 m in the large one) show the least memory. It was noticeable upon recovery of the large probe that the upper one-third was relatively clean, probably attributable to the uncompacted nature of the surface sediments.

Figures 7 and 8 plot lift-out values at the measurement sites made by the two systems. Measurements made using the Hach EC10 Eh meter on core samples from probe sites in the vicinity of Bush Hill are shown in Table 2, and plotted with probe data in Figure 7. Comparisons confirm the satisfactory operation of the remote, autonomous systems. The 60 cm and 3.3 m systems are compared in Figure

Figure 3

Figure 4

Figure 5

Figure 6

8. Comparisons are again satisfactory, with the exception of values recorded by the -20 cm electrode of the 60 cm system at Sites F and G. Eh values in excess of +450 mV are not reported in oxidized marine sediments, but the general tenor of the readings ("highly oxidized") are confirmed by core data at Site F, and 3.3 m system data at F* (Table 2).

Table 2. Eh Measurements, Vicinity of Bush Hill (GC-185) and in MC-664.

Site	Meters N. of Bush Hill	<u>60 cm System</u>			<u>3.3 m System</u>			<u>Cores*</u>	
		-20cm	-40cm	-60cm	-0.65m	-1.65m	-3.15m	-10cm	-30cm
A	50	-46	-193	-160				-173	-200
B	150	-56	-201	-200				-176	-200
C	280	+51	-193	-200					
C*	300				+191	-198	-185		
D	400	+293	-180	-193					
D*	420				+228	-191	-180		
E	520	+433	-145	-134					
F*	465				+292	-178	-180		
F	720	+628	-103	-94				+307	
G	1010	+669	-86	-169				+382	+59
8 (NE)	450				-185	-194	-197		
10 (NE)	680				-197	-199	-200		
1	MC-664				+80	-230	-230		
2	MC-664				+40	-230	-230		
3	MC-664				+20	-230	-230		

DISCUSSION

In summary, the Eh probe systems provided data in keeping with the initially available information, that is, they confirmed the presence of two seepage sites. The sum of the data confirms the validity of the conceptual model of a seepage site in terms of electrical potential shown in Figure 9. The essential concepts of the model are the (1) existence of a normal, regional, background, vertical profile of Eh; (2) the ascent of the sulfide zone (Eh -250 mV) to the surface at the seepage; (3) the existence of compressed vertical gradients in proximity to the seepage; and (4), the existence of horizontal gradients at the surface in the surrounding area. All of these features are represented in the data, except for measurement of the normal vertical gradient. Information in the literature, and from 4 meter cores collected for BP, indicates that reducing conditions are not normally encountered within the upper 3 to 4 m of these deep water sediments. The phenomenon of the sulfide zone rising to the sediment surface at a petroleum seepage was first described by Spies and Davis (Marine Biology, 50, 1979).

Figure 7

Figure 8

Figure 9
Electrical Potential Model of Seepage Site

Figures 1 and 2 demonstrate that the expectable diameters of seepage sites as defined by Eh measurements are equal to, or greater than, 1 kilometer.

The data of Table 2 represent measurements which have provided maximum settling time at each location (two to four minutes), made as the probe was lifted out of the sediment. Settling times are brief, as evidenced by the insertion of a clean probe at Site A in Figure 3. The 60 cm electrode (heavy line) falls from a "drifting" value of +154 mV in sea water, to a sediment reading of -205 mV in 60 seconds, most of which time was required for emplacement. Preliminary tests in Florida coastal waters revealed settling times of the order of 20 seconds.

Sea water in the Gulf of Mexico, specifically in Green Canyon 185 at the sea floor, contains 1 to 3 ml of oxygen per liter. This ensures that all redox systems exist in their most highly oxidized state. Measurements in sea water with the EC10 yielded Eh values of +230 to +250 mV, values which are expectable, therefore, during traverses of the probe systems. However, aberrant values were generally observed. Whitfield (Limnol. & Oceanography, 1969) noted that platinum electrodes are not ideally inert, that their potentials in an oxidizing environment may reflect their condition (e.g. mechanical strain) or previous treatment. They are subject to drift in systems of limited poise, or concentration of redox reactants. On the other hand, reduced sediments are relatively highly poised, exhibiting total sulfide levels of up to 300 mg/l, facts which evidently account for the rapid and consistent responses of the probe electrodes to the negative potentials encountered in reducing sediments. In summary, despite some ambiguous data returned by the probes in oxidizing environments, the systems responded rapidly and correctly when in contact with reducing sediments, which is their intended function.

Depths within the sediment at which measurements were made are accurate for the 60 cm system, the deployment of which was observed visually. The larger system was dropped under gravity. The altimeter attached to the large probe failed to record penetration depth, although it recorded approach to the sea floor and withdrawal. The failure is evidently due to a combination of the effects of mounting geometry (altimeter 90 cm above the base of the pressure vessel), the minimum range

recordable by the altimeter (80 cm), and over-penetration. At least the lower 10 cm of the pressure vessel entered the sediment at each site. Core depths also are slightly uncertain because of sediment loss and compression.

Navigation data for the ship was based upon GPS information. The positions of the 3.3 m probe and of the submarine, relative to the ship, were known at all times to within 30 m. Each carried an acoustic transponder. A corresponding ultra short baseline acoustic navigation system, Trackpoint II (ORE Inc.), was employed on the ship. A computer program combined GPS and Trackpoint data, generating real-time actual and relative position charts.

Future work will be directed towards modifications and marketing. The 3.3 m probe will be fitted with projecting, broadly conical, electrode bases with apically-located platinum contacts upon which it will not be possible to accumulate a film of sediment. Presentation of results to petroleum exploration companies is planned, as well as description in relevant publications and at ocean industry and exploration-oriented conventions.

Acknowledgements

Appreciation is expressed to the staff of the Department of Engineering, Harbor Branch Oceanographic Institution, particularly to A. Clark, Director, F. Caimi, J. Holt, and G. Kennedy, without whose enthusiastic support and contributions this project could not have been accomplished. Work was funded by Grant DE-FG01-95EE15626 of the Energy Related Inventions Program of the U.S. Department of Energy. The system is described in U. S. Patent 5,439,800 of Petrosurveys, Inc.

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October 10, 1996.