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THE IMPACT OF CRAB WASTES ON MARINE ENVIRONMENTS

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THE IMPACT OF CRAB WASTES ON MARINE ENVIRONMENTS

PART I

PROJECT REPORT

Project Title: The Impact of Crab Wastes on Marine Environments

Project No.: F19-82-00815

- Submitted by: Dr. Gregory D. Boardman, Assistant Professor of Civil Engineering Dr. George J. Flick, Professor of Food Science and Technology Ms. Teresa Kramer, Graduate Student, Civil Engineering VPI&SU Blacksburg, VA 24061
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Date: April, 1983

TABLE OF CONTENTS

	ACKN	IOWL	ED	GEM	IEN	ITS	5	_	-				_				_						_			ii
								•	-				•	•	-		•	-	-	•		•	•	-		
	LIST	0F	Ť	ABL	E S								•						•				•			v
	LIST	0F	F	ΙGU	IRE	S										,						,				vi
Ι.	INTR	ODU	CT	ION	۱.				-										•							1
II.	LITE	RAT	URI	ER	EV	ΙE	W		•	•					•		•	•	•	•	•	•	٠	٠	•	4
		_		.																						
		Bur	ia	17L	an	df	i	11	ir	١g	•		•	•	•		•	•	•	•	•	•	•	•	•	10
		Lan	d /	Арр	1 1	ca	t	10	'n	:	•		•	•	•			•	•	•	•	•	•	•	•	12
		Cra	p`l	lea	1	P٣	0	du	C 1	51	o n	1	•	•	•		ı	•	•	•	٠	٠	٠	٠	٠	12
		Off	sh (ore	D	um	I P	in	g	٠	•		•	٠	+			•	•	•		•	•		•	4
		Cha	rac	cte	ri	st	i	c s	C)f	С	r	a b	S	i c	r a	ιр		•	•	•	٠	•	٠	-	16
			SI	nel	1.			•		-	•			•			ı	•	•		•		•			17
			٧.	isc	er	а								•				٠			•	•				17
			Eg	9 9	Ma	\$ S	e:	s	÷																	19
III.	MATE	RIA	LS	AN	D	МE	TI	H0	DS	5			•		•	•			•				•			21
		Fie	1 d	St	u d	ie	S																			
			S	ite	C	h a	ri	ac	tε	r	ίz	a	ti	on	s											21
					Si	te	1	A .																		23
					Si	te	Ē	В					_		-	_										23
					Ŝi	te	(Ċ							Ţ				į		Ż	Ż				23
					ŝi	te	Ī	ñ	•	-	•		•	•	•	•		•	•	•	•	•	•	•	•	26
					ŝi	te	j	F	•	•	•		4	•	•	•		•	•	•	•	•	•	•	•	26
					Ŝi	+ e	Ì	Ē	•	•	•		•	•	•	•		•	•	•	•	•	•	•	•	26
			Si	· ra	J. n	C n	n 1	ta.	; in	•	• •	÷	• • •	• • •	i.		c	•	nd	D	1 =	÷	• • •	• • • +	•	28
			50	- i Lá	Ч		<u>.</u>	1			<u> </u>	L	U	C V		с с	3	ġ	nu	ĩ	ιa	ι,	eme	:100		28
					' J T U	Pe Pe		2	•	•	•		•	•	*	•		•	•	•	•	•	•	•	•	20
			ς ۸		iy n	ne he	~	<u> </u>		÷.	•••	_	' _	Ad	•			• •	2.	:		•	•	•	•	20
			30	. r a	μ ι ~	с т.	ep	Ja	٢đ	ما	10	н	đ	nu	1	ue	μı	03	16	10	ri	•	•	•	·	აა იი
					L () 11	05	е	+ -		٠	٠		•	٠	•	•		•	٠	•	•	•		•	٠	33
					01	C0	ď	ιe J	a	•	•		•	•	•	•		•	•	•	•	•	٠	•	•	33
			ç		60	aτ	ec)	•	•	•		•	•	•	•		•	•	•	•	•	٠	•	•	55
			26	ens	٥r	У	ψt	2 5	e r	٠V	a t	10	חכ	s	•	•		•	•	•	•	•	•	•	٠	34
			Sa	ımp _.	11	ng	ł	r	00	e	du	re	è S		٠	٠		•	•	•	•	•	٠	•	٠	34
]	Wa	te	r		•	•	•		•	•	•	•		•	•	•	•	•	R,	•	٠	34
					Se	dí	m e	en	t	٠	•		,	•	٠	٠		•	•	•	•	•	•	•	٠	35
					Sc	ra.	Ο.	-															_			35

PAGE

II.	MATERIALS	AND	METHODS	(con't)
				(0011 0)

III.	MATERIALS AND METHODS (con't)	
	Tarak Chuddan	PAGE
	Tank and Ambient Conditions	36
	Tanks A. B. and C.	36
	Tanks D. E. F and G.	36
	Scrap Preparation and Deposition	38
	Loose	38
	Compacted	38
	Compacted, Coated	39
	Coated	39
	Analytical Observations	39
	Sensory UDservations	40
	Cadmium Untako Study	41
	All Studies	42 13
	Methods of Measurement and Analysis	43
		10
IV.	RESULTS	49
	Field Studies	49
	Field Study I	49
	Characterization of Sites	49
	Appearance of Scrap	52
	Field Study II	53
	Characterization of Sites	53
	Appearance of Scrap	51
	Characterization of Sites	64
	Annearance of Scrap	64
	Tank Studies	65
	Tank Study I	65
	Sensory Observations	65
	Analytical Observations	70
	Tank Study II	75
	Sensory Observations	75
	Analytical Observations	85
	Oxygen Demand Study	105
	<u>Cadmium uptake Study</u>	108
v	DISCUSSION	119
۰.	Field Studies	119
	Tank Studies	122
	Öxygen Demand Study.	126
	Cadmium Uptake Study	128
	Recommended Disposal Procedure	129
VI.	SUMMARY AND CONCLUSIONS	132
1.J. Y. T		1 2 5
VII.	$K_{E}F_{E}K_{E}NUES, \ldots, \ldots,$	135
T T 7	Annendix	137
	whhenmary	107

LIST OF TABLES

Table		Page
I.	Total annual blue crab landings,in pounds, for Virginia and Maryland, by month, and estimated solid waste generated, 1960 - 1978 (from reference 3).	5
II.	Characteristics of field sites A, B, and C .	50
III.	Characteristics of field sites D, E, and F .	54
IV.	The concentrations of various metals found in the water, sediment,and shell at sites D, E, and F on selected days in June of 1982	62
۷.	Sensory observations made during Tank Study I	66
VI.	Sensory observations made during Tank Study	78
VII.	Results of the BOD ₅ analysis of ground crab scrap using seawater as the testing medium .	106
VIII.	Results of the BOD ₅ analysis of ground crab scrap using BOD dilution water as the test- ing medium	107
IX.	Results of the BOD ₅ analysis of alginate using seawater as the testing medium	109
Χ.	Results of the BOD analysis of alginate using BOD dilution ⁵ water as the testing medium	110
XI.	Results of the COD analysis of ground crab	111
XII.	Results of the COD analysis of alginate	112

e

LIST OF FIGURES

Figure		Page
1.	Percent of the total annual blue crab scrap generated by month in Virginia, 1960 - 1978 averaged (from reference 3)	6
2.	Percent of the total annual blue crab scrap generated by month in Maryland, 1960-1978 averaged (from reference 3)	7
3.	Locations of the blue crab processors in Vir- ginia (from reference 3)	8
4.	Locations of the blue crab processors in Maryland (from reference 3) ,	9
5.	Transverse section of a crab cuticle.(from reference]0)	18
6.	Abdomen of a female blue crab, <u>Callinectes</u> <u>sapidus</u> , with an egg mass beneath the apron	20
7.	Map of the Chesapeake Bay, showing field re- search areas for this study	22
8.	Map of the Lynnhaven Inlet, Virginia Beach, Virginia, Site A	24
9.	Map of the Hampton Roads area of the Chesapeake Bay, Norfolk, Virginia, Site B and Site C	25
10.	Map of the Corrotoman and Rappahannock Rivers, Virginia, Site D, Site E, and Site F	27
11.	Type 1, Scrap Containment Device	29
12.	Type 2, Scrap Containment Device	31
13.	Anchorage of the Type 2, Scrap Containment Device	32
14.	Configuration of the tanks and lids used in the Tank Studies	37
15.	Water temperature and dissolved oxygen varia- tions with depth at Site D at 1615 hours on 5 June 1982	55

vi

Figure

--

--

16.	Water temperature and dissolved oxygen vari- ations with depth at Site D at 1230 hours on 27 June 1982	56
17.	Water temperature and dissolved oxygen vari- ations with depth at Site E at 1730 hours on 5 June 1982	57
18.	Water temperature and dissolved oxygen vari- ations with depth at Site E at 1145 hours on 27 June 1982	58
19.	Water temperature and dissolved oxygen vari- ations with depth at Site F at 1820 hours on 5 June 1982.	59
20.	Water temperature and dissolved oxygen vari- ations with depth at Site F at 1040 hours on 27 June 1982	60
21.	Concentrations of Cd and Zn found in the water, sediment, and shell at Site D, Site E, and Site F	63
22.	Daily variations in the concentration of NH ₃ in the water in Tanks A, B, and C during the first six days of Tank Study I	71
23.	Daily variations in the turbidity of the water in Tanks A, B, and C during the first six days of Tank Study I.	7.3
24.	Daily variations in the concentration of TOC in the water in Tanks A, B, and C during the first six days of Tank Study I	74
25	Daily variations in the concentration of BOD in the water in Tanks A, B, and C during the first six days of Tank Study I	76
26	The variations in the concentrations of nitro- gen containing compounds in the water in Tank D on the sampling days of Tank Study II.	97
27.	The variations in the concentrations of nitro- gen containing compounds in the water in Tank E on the sampling days of Tank Study II	88

Figure

gure		Page
28.	The variations in the concentrations of nitro- gen containing compounds in the water in Tank F on the sampling days of Tank Study II	89
29.	The variations in the concentrations of nitro- gen containing compounds in the water in Tank G on the sampling days of Tank Study II	90
30.	The variations in the concentrations of nitro- gen containing compounds in the water in Tanks D, E, F, and G on the sampling days of Tank Study II	9]
31.	The variations in the concentration of TOC in the water in Tank D on the sampling days of Tank Study II	93
32.	The variations in the concentration of TOC in the water in Tank E on the sampling days of Tank Study II	94
33.	The variations in the concentration of TOC in the water in Tank F on the sampling days of Tank Study II	95
34.	The variations in the concentration of TOC in the water in Tank G on the sampling days of Tank Study II	96
35.	The variations in the turbidity, pH, and the dissolved oxygen concentration in the water in Tank D on the sampling days of Tank Study II .	98
36.	The variations in the turbidity, pH, and the dissolved oxygen concentration in the water in Tank E on the sampling days of Tank Study II.	99
37.	The variations in the pH and the dissolved oxygen concentration of the water in Tank F on the sampling days of Tank Study II	100
38.	The variations in the pH and the dissolved oxygen concentration of the water in Tank G on the sampling days of Tank Study II	101

Fi	gu	re
----	----	----

39.

40.

The variations in the turbidity of the water in Tank F on the sampling days of Tank Study II	103
The variations in the turbidity of the water in Tank G on the sampling days of Tank Study II	104

Page

		104
41.	Uptake of Cd by craɓ shells over an eight day period	114
42.	Uptake of Cd by 8 g of crab shell over an eight day period	115
43.	Uptake of Cd by 16 g of crab shell over an eight day period	116
44.	Uptake of Cd by 32 g of crab shell over an eight day period	117
45.	Levels of Cd adsorbed by various amounts of crab shell after eight days	118

I. INTRODUCTION

Many years ago the crab processing industry disposed of crab waste by dumping it into the natural waters adjacent to their processing plants. This was the most convenient and inexpensive method of disposal. The only cost was for an occasional dredging of the dumping area to remove the accumulated shell material.

Some processors took this disposal method a step further and used the waste as a resource. They would choose a spot in the water away from the dock to dump the wastes. Dumping in this area would proceed over a period of one week to a month. By the end of that time, the area would have become a feeding ground for eels. A week after the dumping had stopped, eel traps were placed in the area and the harvest began. (1)

As environmental concerns heightened, legislative and enforcement actions were taken to stop the dumping of crab processing wastes into public waters of Virginia and Maryland. Most of the complaints filed against the disposal method were aesthetically based, e.g., visible floating debris, odor problems, and increased turbidity. No formal research was conducted to assess the environmental impact of the method.

After the banning of offshore dumping in 1972, the crab processing industry turned to three alternatives. These were burial/landfilling, agricultural land application, and crabmeal production. Of these, crab-meal production, until

recently, was the most economically and environmentally sound method of crab waste disposal. However, rising interest rates and building costs and the falling market price of crab-meal have resulted in either the postponement or cancellation of construction plans for additional crab-meal processing plants. With crab-meal production severely handicapped and landfilling options being cut back, attention has turned to the revitalization of offshore dumping.

The objective of this study was to evaluate the problems associated with offshore disposal of crab scrap and to develop a means of handling the crab scrap which would minimize these problems.

Scope of Study

The first topic addressed in this research was the identification of a method of scrap preparation that would reduce the volume of the crab scrap, reduce odor during scrap handling, prevent floating scrap, and be easily and inexpensively implemented by the crab processors. Four methods of scrap preparation were tested. Two involved just the scrap and two involved an alginate coating for the scrap. A sample of each of the scrap preparations was then tested in the laboratory to determine the degree to which the aforementioned criteria were met. The effects of the

scrap on water quality were also examined. Laboratory analyses of the oxygen demand exerted by the degradation of the scrap and the alginate were performed. The two methods of scrap preparation which seemed to best meet the criteria were then tested in the field in an attempt to determine the dispersion/degradation rate of the scrap.

Also of interest was the adsorptive capacity of the shell material for heavy metals. This was investigated through both field and laboratory studies. During one of the field studies, shell, sediment, and water samples were taken for analysis of selected metals. In a laboratory study, the ability of the shell material to adsorb cadmium was investigated.

II. LITERATURE REVIEW

Crabs are this nation's fourth most valuable fishery, surpassed only by shrimp, salmon and tuna (2). Approximately one-half of the crab harvest is comprised of the blue crab (<u>Callinectes sapidus</u>) and, of the blue crabs landed nationally, 50 percent are taken from the Chesapeake Bay area (2). This means that between 50 and 80 million pounds of crabs are harvested from the Chesapeake Bay area each year (Table I) (3).

Along with this valuable industry comes a major waste disposal problem. Approximately 70 percent, by weight, of the crab harvest becomes waste material (3). This solid waste is primarily the inedible shell and viscera of the crab.

Crab waste is produced not only in large amounts but also with a high degree of seasonal variability and in localized areas (3). In Virginia, over 55 percent of the annual crab scrap is generated in the five months from June through October (Figure 1). In Maryland, the seasonal generation of scrap is even more pronounced, with 88 percent of the annual crab scrap generated in the five months from June through October (Figure 2). Figures 3 and 4 show the areas in Virginia and Maryland, respectively, where 50 to 80 million pounds of crabs are processed annually. The Virginia industries process approximately 66 percent of these crabs, thus

Virginia	Maryland	Total
5,069,589	4,215,256	9,284,845
4,776,336	3,047,887	7,824,223
2,202,381	896,099	3,098,480
4,199,626	99,133	4,298,759
2,705,689	1,133	2,706,822
2,040,510	793	2,041,303
1,402,438	1,384	1,403,822
2,402,127	377,972	2,780,099
3,652,328	1,159,042	4,811,370
4,677,860	3,028,147	7,706,007
5,317,491	5,082,731	10,400,222
5,666,528	5,124,676	10,791,204
4,112,903	23,034,253	67,147,156
80,879,032	16,123,977	47,003,009
9,925,403	5,182,707	15,108,110
	5,069,589 4,776,336 2,202,381 4,199,626 2,705,689 2,040,510 1,402,438 2,402,127 3,652,328 4,677,860 5,317,491 5,666,528 4,112,903 30,879,032 9,925,403	5,069,589 $4,215,256$ $4,776,336$ $3,047,887$ $2,202,381$ $896,099$ $4,199,626$ $99,133$ $2,705,689$ $1,133$ $2,040,510$ 793 $1,402,438$ $1,384$ $2,402,127$ $377,972$ $3,652,328$ $1,159,042$ $4,677,860$ $3,028,147$ $5,317,491$ $5,082,731$ $5,666,528$ $5,124,676$ $44,112,903$ $23,034,253$ $30,879,032$ $16,123,977$ $9,925,403$ $5,182,707$

TABLE I. TOTAL ANNUAL BLUE CRAB LANDINGS IN POUNDS FOR VIR-GINIA AND MARYLAND, BY MONTH, AND ESTIMATED SOLID WASTE GEN-ERATED, 1960 - 1978 (FROM REFERENCE 3).

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Figure 1. Percent of the total annual blue crab scrap generated by month in Virginia, 1960-1978 averaged (from reference 3).



Figure 2. Percent of the total annual blue crab scrap generated by month in Maryland, 1960-1978 averaged (from reference 3).



Figure 3. Locations of the blue crab processors in Virginia (from reference 3).



Figure 4. Locations of the blue crab processors in Maryland (from reference 3).

producing 66 percent of the crab scrap, while the Maryland processors produce the remaining approximately 34 percent of the crab scrap. The problem of localized production of crab scrap may be illustrated by the fact that 66 percent of the crab scrap produced in Maryland, or approximately 10.5 million pounds per year, is produced by the processors located in the 350 square miles due west of a line extending from Cambridge to Stockton (4). Both the seasonal variability and the localized production of the crab scrap combine to severely restrict the waste disposal options.

In the following sections, the four major scrap disposal methods currently in use are described. They are: burial/ landfilling, agricultural land application, crab-meal production and offshore disposal. The advantages and disadvantages of each method are discussed. The character of the crabprocessing wastes is also described in the final section of this chapter.

Burial/Landfilling

The use of a landfill or dump is a convenient, inexpensive disposal method. The only costs incurred by the processor are those of hauling and landfill fees. It would seem to be a viable option where either ample land suitable for sanitary landfills or landfills licensed to accept putrescible matter are available.

However, it has been found that crab scrap is a very difficult material to landfill. The "drip" from the transport truck causes insect - and odor problems along the route to the landfill (5) and has alienated many communities. The odor generated by crab scrap has been a major problem for landfill personnel who must remain at the landfill site for ten hours at a time (6). Even though the scrap comes into the landfill fresh and is immediately covered, the volatile gases produced during the decomposition of the crab meat cause cracking of the cover material, resulting in odor problems (4).

Another major problem with crab scrap disposal at landfills is the large volumes involved. One landfill in Somerset County, Maryland estimated that they would be required to accept 7000 cubic yards of crab scrap in 1980 (6). This annual volume would markedly decrease the useful life of most landfills in the vicinity of crab processors. Also, the intermittent cover for this volume of scrap required the expensive hauling of extra cover material which, in turn, placed an additional tax burden on the county residents (6).

George Miles, supervisor of Somerset County Landfill, has stated, "In Somerset County we would appreciate any alternative to disposal in our landfills" (6). Other municipal and private landfill operators are sure to share this position.

11

Land Application

Many crab processors have the scrap disked into fields as a crude fertilizer for grasses and crops. This has been common practice in the central and upper Chesapeake Bay for many years and, if properly managed, is a viable disposal method in the spring before the crops have been planted or in the fall after the crops have been harvested (4). Unfortunately, the majority of the crab scrap is produced after the farmland has been planted (Figures 1 and 2).

This method also cannot be used when the ground is too wet for tilling. The scrap must be turned under immediately after application to realize the maximum fertilizer value (4). If allowed to remain on the surface, severe odor and pest problems result.

Another problem which has recently become evident is the subdividing of farm lands into residential plats and developments. The land application method of scrap disposal requires large areas of agricultural fields away from residential areas. The current expansion of residential housing into agricultural farm land may therefore preclude this method of disposal.

Crab_Meal Production

This is the most recently developed disposal technique and is more a resource recovery technique than a disposal

method. It involves the dehydration and pulverization of the scrap to form a crab-meal which is sold for use as a protein supplement poultry feed.

In 1979, when crab-meal prices were high (\$146 per ton) and energy costs relatively low, this method of disposal/ resource recovery was not only environmentally sound, but was also profitable (1). However, since energy costs have increased and crab-meal prices have decreased to a level of \$100 per ton in 1982, this method is no longer profitable (1). This decrease in the price of crab-meal was required so that crab-meal would remain competitive with the grains used in poultry feeds. The prices of these grains had decreased markedly in 1981 and 1982. Another point of competition between crab-meal and feed grains is the consistency of supply (1).

It has always been difficult for crab-meal processors to provide the producers of poultry feed with a consistent supply of crab-meal because the production of crab scrap is so variable from year to year and season to season. This yearly and seasonal variability is also seen in grain production, but most farmers have solved this problem by forming a grain co-operative to store grain until it was needed. It follows that crab-meal processors should be able to remedy their supply problems by forming a similar co-operative for storage of crab-meal (1).

13

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In areas where there are no crab-meal production facilities, this disposal technique is not feasible. With current high interest rates and construction and machinery costs, the present price of the crab-meal does not come close to warranting the construction of new facilities (1).

Offshore Dumping

Currently, South Carolina is the only state which issues National Pollutant Discharge Elimination System (NPDES) permits for controlled dumping of crab scrap (5). They allow several crab processors "to dump at designated water areas in the vicinity possessing adequate depth, flow and/or marine life to adequately absorb the solids and/or have a beneficial impact upon the surrounding ecosystems" (5). According to John Ohlandt, of the Charleston office of the South Carolina Department of Health and Environmental Control (SCDHEC), there are no specific regulatory criteria or standards governing site selections for the offshore disposal of crab scrap. The decision to allow crab scrap dumping in a particular area is left to the discretion of the SCDHEC agent (7).

This has been a major step toward solving the disposal problem. Even though a NPDES permit is required, an Environmental Protection Agency (EPA) ocean dumping permit is not. This is because fish wastes are excluded from the Federal ocean dumping and permit requirements and fish wastes are

defined by the EPA as the returning to the sea of any unadulterated (without additive) seafood wastes (8).

Arguments in support of this disposal method center around the fact that it returns nutrients to nutrient deficient portions of the sea for support of marine ecosystems. The contention is that the process recycles products taken from the sea in a manner similar to the natural process of death and decay in the sea (8).

Section 74 Seafood Processing Study Executive Summary (9) was the only research found which addressed the environmental impact of the disposal of crab scrap in a marine environment. This study mainly addressed the direct piping of seafood wastes from the processing plants into the adjacent waters. This differs greatly from offshore disposal, but will be addressed in this section, as it is apparently the only related research available.

The environmental impacts which these researchers identified were highly site specific. The sites used were located in the Dutch Harbor, Cordova, and Kenai areas of Alaska. The worst impacts were found in the Dutch Harbor area of Alaska. This is a very confined harbor which has very restricted circulation patterns and a heavy volume of processing activity. The negative impacts experienced in this area were high ammonia, hydrogen sulfide, and phosphorus concentrations, low dissolved oxygen concentrations, large

accumulations of wastes, and some floating matter (9).

The Cordova sites exhibited better circulation patterns than those seen in Dutch Harbor, however, they were still quite restricted. One processor in this area had been dumping whole crab scrap from the dock. The water around the dock exhibited a slight surface discoloration and floating debris was observed. The accumulation of waste seemed to be restricted to an area within five meters of the dock. Despite these waste accumulations, Cordova's water quality was generally good (9).

In evaluating the Alaskan studies, the U.S. Fish and Wildlife Service concluded that these investigations were too brief and localized to support definite conclusions. However, the study did help to identify the major concerns which have been associated with crab scrap disposal in a marine environment (9).

Characteristics of Crab Scrap

Reports of studies characterizing crab processing scrap are not available. However, it is known that the scrap is comprised mainly of shell, viscera and egg masses. The character of these crab parts and, consequently, the predominant characteristics of the crab scrap can be predicted rather accurately from anatomical knowledge of crabs.

Shell

The exoskeleton or shell is a tough cuticle which is heavily calcified over most of the outside of the body. It is composed of four layers: epicuticle, exocuticle, endocuticle and membranous layer (Figure 5) (10).

The epicuticle is the outer layer and is the only layer of the shell which does not contain chitin. It is made up of lipo-protein. It is not as heavily calcified as the other layers and retains some flexibility (10).

The exocuticle and endocuticle layers are similar. They both contain matrixes of chitin-protein microfibrils. These microfibrils are arranged in such a way as to impart great strength to the shell. Both layers are strengthened by heavy calcification of this chitin-protein matrix.

The innermost layer is the membranous layer which is similar to the endocuticle in construction, but is uncalcified. It appears as a cellophane-like sheet covering the interior of the endocuticle (10).

Viscera

The viscera is comprised of the gills, bladder, heart, stomach, intestines and hepatopancreas. These are all organic in nature and form the readily degradable/putrescible portion of the scrap (10).



Figure 5. Transverse section of a crab cuticle (from reference 10).

Egg Masses

The appearance of egg masses in crab scrap is seasonal. They generally appear attached to the female crab in late spring and early summer throughout the lower reaches of the Chesapeake Bay.

These egg masses are bright orange, spongy and are found under the apron on the ventral surface of the female (Figure 5).



Figure 6. Abdomen of a female blue crab, <u>Callinectes</u> $\frac{\text{sapidus}}{\text{apron.}}$, with an egg mass beneath the

III. MATERIALS AND METHODS

Field Studies

Site Locations and Characteristics

Sites A, B, and C were located in the Hampton Roads area of the Chesapeake Bay. This area is located just inside the mouth of the Chesapeake Bay, near Virginia Beach and Norfolk, Virginia. This area was chosen so that three sites could be selected which would vary widely in salinity, yet still be in close proximity to one another. These sites were used for Field Study I.

Sites D, E, and F were located in the Corrotoman River, which feeds into the Rappahannock River. This area is located near Irvington, Virginia, and is approximately 100 kilometers inside the mouth of the Chesapeake Bay (Figure 7). These sites were used for both Field Studies II and III.

In order to characterize conditions at each site, observations were made, measurements were taken and analyses were performed. Among the data collected were date, time, weather and sea conditions, times of tides, depth, type of sediment, current velocity, salinity, Secchi readings, pH, water temperature, dissolved oxygen (D.O.), organic nitrogen, ammonia (NH₃), nitrite/nitrate ($NO_2^2+NO_3^2$), alkalinity, total organic carbon (TOC), turbidity, lead (Pb), arsenic (As), mercury (Hg), cadmium (Cd), and zinc (Zn).



Figure 7. Map of the Chesapeake Bay, showing field research areas for this study.

Site A

Site A was directly outside the mouth of the Lynnhaven Inlet, Virginia Beach, Virginia (Figure 8). Two crab scrap containers were anchored in line with and between navigational marker number three and the tip of the Lynnhaven sandbar. An empty control container was anchored ten meters (m) due east of the crab scrap containers.

This site was chosen for its high salinity of 20 parts per thousand (ppt), its high tidal velocity, and its firm sandy bottom.

<u>Site B</u>

Site B was 150m due west of the tip of Willoughby Spit, Norfolk, Virginia (Figure 9). Two crab scrap containers were anchored midway between the navigational marker and the Hampton Road Tunnel Bridge. An empty control container was anchored 10m due north of the crab scrap containers.

This site was chosen for its moderate salinity of 14 ppt, its moderate-to-high tidal velocity, and its firm mud bottom.

Site C

Site C was in the Lafayette River in Norfolk, Virginia (Figure 9). Two crab scrap containers were anchored midway between the Granby Street Bridge and the Willow Wood Bridge, 15m offshore. An empty control container was anchored 10m



Figure 8. Map of the Lynnhaven Inlet, Virginia Beach, Virginia, Site A.


northeast of the crab scrap containers,

This site was chosen for its low salinity of 11 ppt, its moderate tidal velocity, and its muck bottom.

Site D

Site D was in the Corrotoman River, near Bar Point. Two crab scrap containers were anchored 15m northeast of navigational marker R2 (Figure 10). No control container was placed at this site.

This site was chosen for its low current velocity and its relatively shallow depth of approximately 4.5m.

Site E

Site E was in the Corrotoman River, near Taylors Creek. Two crab scrap containers were anchored 30m east of navigational marker R4 (Figure 10). No control container was placed at this site. This site was chosen for its low current velocity and its depth of approximately 6.0m.

<u>Site F</u>

Site F was just inside the mouth of the Corrotoman River. Two crab scrap containers were anchored midway between navigational marker M2 and the western shoreline. No control container was placed at this site.

This site was chosen for its low-to-moderate current



velocity and its depth of approximately 10 m.

Scrap Containment Devices and Placement

Type 1

The Type I scrap containment device was designed to allow the scrap to be raised and lowered without any loss of scrap. Once on the bottom, the sides would fold down and expose the scrap to the surroinding environment (Figure 11).

Materials used in the construction of this device were relatively inert in the marine environment. The main body was formed from an extruded plastic mesh framework, with plastic ties used for hinges. Fiberglas screening (42 square per square centimeter (cm)) was attached to the interior walls of the plastic mesh by melting a portion of the plastic mesh around the screening and allowing it to harden. No metals or adhesives were used in the device,

Three of these Type 1 devices were placed at each of the three sites: Sites A, B, and C. Two were used for scrap containment and one remained empty, to be used as a control.

Type 2

The Type 2 scrap containment device was designed to allow water to flow through while retaining as much scrap as possible. To accomplish this, 20 holes of 2.5 cm in



diameter were drilled at 5 cm intervals in the sides of a 25 liter (L) carboy (Figure 12). A 12 cm square door was cut in the side, leaving one corner attached to act as a hinge. Two 2.5 cm diameter holes were drilled in the bottom to allow water to drain as the device was retrieved from the water.

Fiberglas screening was sewn with nylon fishing line to form a tight-fitting sack enclosing the carboy. The sack was designed to tightly cover all holes and the door, and was fastened with a drawstring to the handles of the carboy (Figure 12). This fiberglas screening had 42 squares per square cm. This mesh allowed only particles smaller than 1.5 by 1.7 millimeters (mm) to escape.

The anchoring system consisted of two 7.5 kilogram (kg) base weights at each site. These base weights were attached to the two carboys by a single length of line equivalent to the maximum depth at each site, so that the achor remained in place during container retrieval (Figure 13). One additional 1.5 kg weight was attached to the neck of each carboy. These weights were exercise weights made of Orbitron, a white plastic, and filled with sand.

Two carboys were tied together and placed at each of the three sites: Site D, E, and F. A line attached to these carboys lead to a flat, square piece of white styrofoam at the water's surface which served as the marker float. Ample line was used between the float and the carboys to pre-





vent the submergence of the floats at high tide.

Scrap Preparation and Deposition

Three forms of crab scrap were used in the field studies: loose, coated, and uncoated. The loose scrap was taken directly from the processing plant and not altered in any way.

The coated and uncoated scrap were prepared as follows. Loose scrap was ground in a meat grinder using a 0.25-inch cutting plate. The scrap was then weighed into 500 gram (g) quantities. These were formed, by hand, into scrap balls.

Some of the scrap balls were sprayed with a coating of a one percent. (by weight) solution of Low Viscosity Kelgin (L.V., Kelco, Chicago, Illinois), an alginate. This was followed by a spray of a five percent (by weight) solution of calcium chloride (CaCl₂) in distilled, deionized water. The CaCl₂ solution causes the alginate to gel. After air drying for 30 minutes, the coated scrap balls were dry enough to handle.

The reaction which occurs between the alginate (Na_2Alg) and the CaCl₂ to cause gelling is as follows: $Na_2Alg + CaCl_2$ = CaAlg + $2Na^+$ + $2Cl^-$. The CaCl₂ reaction occurs first with the outer layer of alginate molecules and then slowly proceeds to the inner layers if adequate CaCl₂ is applied. The use of sprays as opposed to other methods of application

prevents the trapping of ungelled alginate beneath the outer alginate coating.

Five coated scrap balls were placed in one scrap container at each site for each of the three field studies (I, II, and III). Five uncoated scrap balls were placed in one scrap container at each site for Field Studies I and II. A 2500 g mound of loose scrap was placed in one scrap container at each site in Field Study III.

Sensory Observations

The condition of the crab scrap was visually observed at each site on each sampling date. These observations were made to determine the extent of degradation and/or dispersion of the crab scrap. Observations were made at Site A on May 2 and 15, 1982, and at Sites B and C on May 1, 2, and 15, 1982, in Field Study I. Observations were made at Site D, E, and F on June 5, 6, 15, and 27, 1982, in Field Study II, and July 17, 19, 21, and 23, 1982 in Field Study III.

Sampling Procedures

Water Sampling

The water at each site was sampled using a Van Dorn sampling bottle. Each sample was taken at a depth of 0.5 m from the bottom to avoid entraining sediment with the water

sample. After sampling, the water was placed in appropriately marked sample bottles. Water samples were taken from Site A on May 2 and 15, 1982, and Sites B and C on May 1, 2, and 15, 1982. Water samples were taken from Sites D, E and F on June 5 and 27, 1982.

Sediment Sampling

Bottom sediment samples were taken from each site using an Eckman dredge. These samples were removed from sediment which had not come in contact with the dredge, in an effort to prevent contamination from the dredge. Sediment samples were taken from Sites A, B, and C on May 2, 1982. Sediment samples were taken from Sites D, E, and F on June 5 and 15, 1982.

Scrap Sampling

The containment device was raised to the surface and once the water drained from the device, it was opened and a visual observation of the scrap was made. The scrap was then sampled with a polyethylene cup to avoid possible contamination. Scrap samples were taken from Sites D, E and F on June 5, 6,15, and 27, 1982.

Tank Studies

Tank and Ambient Conditions

The tanks used in these studies were 114 L (30 gallon) glass aquaria. These tanks were fitted with Plexiglas lids to prevent the escape of excessive odor to the laboratory and to enhance anaerobic conditions in those tanks which were non-aerated (Figure 14). The lids were equipped with ports for sampling and venting (in the aerated tanks). The lids were sealed to the lip of the tanks with tape.

Tanks, lids, and all aeration tubing and stones were washed thoroughly with Alconox and water and then rinsed with tap water and distilled, deionized water. The tanks were then placed on laboratory tables in a location out of direct sunlight and away from windows to reduce temperature variations. Each aerated tank was equipped with rubber tubing and a single coarse aeration stone for aeration. The laboratory central air supply was filtered through glass wool filter before being introduced into the tanks.

Tanks A, B, and C

Tanks A, B, and C were used in Tank Study I and all were set up in a similar manner. Each of the three tanks was filled with 100 L of tap water. Aeration was begun and continued for 48 hours in order to dissipate the chlorine





residual, saturate the water with D.O., and allow the water to equilibrate. The tanks were then ready for the scrap.

Tanks D, E, F, and G

Tanks D, E, F, and G were used in Tank Study II. They were all filled with 100 L of saline water from the Corrotoman River. Enough sediment from Site D was then added to Tanks E and F to form a five cm layer on the bottom. The aeration stone in Tank E was positioned one inch above the sediment. Then aeration was begun in Tanks D and E. All the tanks were allowed to sit undisturbed for 48 hours to allow the sediment to settle and the systems to equilibrate.

Scrap Preparation and Deposition

Raw crab scrap was obtained from the RCV Seafood Corporation plant located in Morratico, Virginia. It was bagged at the plant immediately after picking and held at approximately four degrees centigrade (4° C) during transit to the Food Science and Technology Laboratory in Blacksburg, Virginia, where it was stored at 4° C. Three hundred grams of this raw scrap were dropped into Tank A.

A compacted scrap block was formed by cutting 300 g of the "as received" scrap into pieces smaller than ten cm square. Half of this cut scrap was placed in a cylindrical steel cell, three inches in diameter and eight inches

deep with small holes, 0.2 cm in diameter, in the sides to allow air and liquid to escape. A force of 27,600 kilopascals (4000 pounds per square inch (psi)) was then applied with a piston to compact the scrap. Pressure was released and the remainder of the cut scrap was then placed in the cylinder, on top of the other scrap. The same pressure was reapplied. During compaction, approximately 60 milliliters (ml) of fluid was lost. The weight of the scrap, after compaction, was 163 g. This compacted block was dropped into Tank B.

The compacted, coated scrap block was formed in the same manner as the compacted scrap block. However, after compaction it was then spray coated with an alginate gel. This compacted, coated scrap block was then dropped into Tank C.

Coated scrap balls were formed by the same method used to prepare the coated scrap balls for the Field Studies, except 300 g of ground scrap was used rather than the 500 g used in the Field Studies. One coated scrap ball was dropped into each of Tanks D, E, F, and G.

Analytical Observations

Measurements in Tank Study I were made on days 0, 1, 2, 3, 4, 5, and 6. The parameters measured were water temperature, D.O., turbidity, BOD_5 , TOC, pH, and NH_3 . The water samples for these tests were removed from the tank with a

100 ml pipet. The samples, unless otherwise specified, were removed in such a way as to be representative of the water column. This was accomplished by starting to remove the sample near the bottom of the tank and then slowly pulling the pipet up through the tank at a constant rate so that the pipet was full when it reached the surface.

The measurements for Tank Study II were made on days 0, 1, 2, 3, 5, 7, 9, 11, 13, 16, 19, 22, 29, and 36. The parameters measured were NH_3 , organic nitrogen, oxidized nitrogen $(NO_2^- + NO_3^-)$, TOC, D.O., pH, turbidity, and water temperature. The water samples for these tests were removed from the tank with a 100 ml pipet. The samples, unless otherwise specified, were removed as previously described. Samples for turbidity measurements were taken from the bottom and upper portions of the tanks when the tanks visually exhibited turbidity stratification.

Sensory Observations

The sensory observations made during Tank Study I were made daily for 17 days for Tanks A and B, and for 36 days for Tank C. These observations were the appearance of the scrap, the odor of the water, and the color and appearance of the water.

The sensory observations made during Tank Study II were made on days 0, 1, 2, 3, 5, 7, 9, 11, 13, 16, 19, 22, 29,

and 36. The observations included the appearance of the scrap, the odor of the water, floating matter, biological growth, and the color and appearance of the water.

Oxygen Demand Study

The five-day biochemical oxygen demand (BOD₅) of the ground scrap and alginate was analyzed using both seawater (from the Corrotoman River) and dilution water as diluents. The dilution water used in this study was the same as the dilution water used in the BOD₅ analysis performed in the Tank Studies.

Analysis of the chemical oxygen demand (COD) of the ground scrap and alginate was performed using only distilled water as the dilution medium. Seawater was not used for the COD analysis because Standard Methods(11) indicates that the COD analysis is not accurate when the sample has a salinity greater than two parts per thousand (ppt).

For the analysis of BOD₅ in this study, the Hach Manometric BOD apparatus was used. A detailed explanation of the Hach procedure may be found in Appendix A. Predetermined weights of the ground crab scrap were placed in each of the BOD bottles and then 157 ml of either seawater or dilution water was added. The amounts of scrap used were 0.1, 0.2, 0.4, and 0.5 g when seawater was used and 0.1 and 0.4 g when dilution water was used. Alginate solutions of 2.5 g/L and 5.0 g/L were made with dilution water. The Hach BOD analysis was then performed on each of these solutions.

The procedure outlined in Section 508 of <u>Standard</u> <u>Methods</u> was used for the analysis of COD in this study (11). For the scrap analysis, 0.05 and 0.10 g of scrap were analyzed. For the alginate analysis, solutions of 0.5 g/L and 1.0 g/L were analyzed.

Cadmium Uptake Study

The adsorptive capacity of crab shell material for Cd was studied. All of the glassware used in this study was cleaned with Alconox and water, a 50 percent hydrochloric acid (HCl) solution, a 50 percent nitric acid (HNO₃) solution, and then rinsed three times with distilled, deionized water.

Twenty-four 300 ml BOD dilution bottles were arranged on a shaker table. Clean, broken pieces of blue crab carapace were placed in the BOD bottles as follows: 0.5 g in each of three bottles, 1.0 g in each of three bottles, 2.0 g in each of three bottles, 4.0 g in each of three bottles, 8.0 g in each of three bottles, 16.0 g in each of three bottles, 32.0 g in each of three bottles, and no scrap in three bottles. A two milligram (mg) per liter solution of Cd was prepared with seawater from the Rappahannock River;

and, 200 ml of this solution were placed in each bottle. The 24 bottles were then stoppered and shaken for eight days.

Ten ml aliquots were removed from each bottle after one, two, four, six, and eight days of agitation. Each aliquot was acidified with 0.1 ml of concentrated HNO₃ and analyzed for Cd using an atomic absorption spectorphotometer in the flame detection mode.

All Studies (As Applicable)

Methods of Measurement and Analysis

Information concerning the weather conditions and tides was obtained from the United States Weather Service. The Weather Service continually broadcasts weather and tidal information on certain frequencies in the coastal areas.

Depth was measured using a sounder. This sounder was made of nylon line which was marked in half-meter increments and connected to a two-pound lead weight. The weight was lowered slowly into the water until it reached the bottom and then the depth was read at the surface.

Current velocity was measured using a pygmy current meter (Gurley Corporation, Troy, New York). These measurements were taken at a depth equal to three-fifths of the depth at the site (except Site F, where it was taken at a depth of 4 m). This depth at each site was used in an effort to obtain the most representative current velocity at the sampling time.

Salinity was measured using a Yellow Springs Instruments Salinity, Conductivity and Temperature (YSI-SCT) meter (YSI, Yellow Springs, Ohio). This meter was calibrated at the site in distilled, deionized water. Salinity measurements were made at the site on water taken from the surface and bottom of each site. If these readings did not differ by more than one ppt, only the average value was reported.

A Secchi disk reading was made at each site to determine the transparency of the water. A 12-inch Secchi disk attached to a nylon line marked in half-meter increments was used.

The pH of the water was measured using a Fisher Model 640 Accumet Mini pH/mV Meter. Measurements of pH were made in the field on both surface and bottom water samples. If these readings did not differ more than 0.5 pH units, only the average value was reported. The pH readings in the Tank Studies were taken three inches below the water's surface.

Water temperature and D.O. were measured using a YSI D.O. and temperature meter (YSI, Yellow Springs, Ohio). This instrument was calibrated in ambient air before use. In the field studies, the probe was weighted with a one pound lead weight. At Sites A, B, and C, the D.O. of bottom water samples was determined. For Sites D, E, and F,

D.O. readings were taken at depths of 0.5 and 1 m, and 1 m intervals thereafter.

The alkalinity analysis was performed in the field and laboratory according to Section 403 of Standard Methods (11).

The remaining measurements and analyses were conducted using samples which were taken from the field sites or the tanks and preserved. Each sample, with the exception of the TOC sample, was placed in a polyethylene container and then preserved in the manner appropriate for the analysis to be made. The TOC samples were placed in clean glass jars which could be capped to prevent contamination.

All samples were kept at a temperature of 4⁰C until the analyses were performed. All equipment was calibrated in accordance with manufacturers specifications.

Samples to be analyzed for ammonia and $NO_2^- + NO_3^-$ were preserved with 0.2 ml of 1 molar (M) HCl per 200 ml of sample. This preservation technique was suggested in the manual provided with the Orion ammonia probe.

To measure the ammonia concentration, 10 ml of sample were placed in a screw-top vial with a stir bar and 0.2 ml of 10 M NaOH was added. The Orion ammonia probe was inserted and the "actual" ammonia concentration in mg/L as N was read from the Orion 407A specific ion meter. To analyze for the NO_2^- + NO_3^- levels (12), 0.2 g of Devarda's alloy was placed in a 25 ml glass vial with a screw top which contained

10 ml of sample and 0.2 ml of 10 M NaOH. This vial was then capped, placed on a shaker table and agitated for 20 minutes. It was then placed in a water bath at room temperature for ten minutes to allow the sample to equilibrate. A stir bar and the ammonia probe were then placed in the vial and a reading in mg/L as N (reading = total ammonia concentration = $NH_3 + NO_2^2 + NO_3^2$) was taken while the solution was stirred. The $NO_2^2 + NO_3^2$ concentration in mg/L as N was calculated by subtracting the "actual" ammonia concentration reading from the total ammonia concentration reading. This difference was the amount of NH_3 which had been produced by the reduction of $NO_2^2 + NO_3^2$.

Samples to be analyzed for organic N were preserved with 0.2 ml of concentrated sulfuric acid (H_2SO_4) per 200 ml of sample as suggested in Section of 420B of <u>Standard Methods</u> (11). The concentration of organic N in mg/L as N was determined by first analyzing for the total Kjeldahl N (TKN) in the sample. This was done using the micro Kjeldahl procedure as described in Section 420B of <u>Standard Methods</u> (11). The organic N concentration in mg/L as N was then calculated by subtracting the ammonia concentration from the TKN value.

The turbidity of the samples was measured using a Hach turbidimeter and the manufacturer's recommended procedure.

Water samples taken during Tank Study I were analyzed for BOD₅ using the method outlined in Section 507 of

<u>Standard Methods</u> (11). The seed for the dilution water used in this analysis was obtained from laboratory-scale biological reactors which were seeded with municipal sewage and maintained on solutions of dog food.

Water samples analyyzed for TOC were preserved by the addition of 0.1 ml of concentrated phosphoric acid (H_3PO_4) per 50 ml of sample (11). These samples were then analyzed using an Oceanographic TOC analyzer (Oceanographic Instrument Corporation, College Station, Texas).

Water samples for the analysis of selected metals were preserved by adding 1 ml of concentrated HNO₃ per liter of sample (11). These samples were then analyzed for Pb, As, Cd, Hg, and Zn using an atomic absorption spectrophotometer.

Sediment samples taken in Field Study II were processed in the following manner prior to an analysis for associated Cd, Zn, Hg, Pb, and As levels. The sediment was placed in a cardboard box and placed on a shelf in the laboratory to allow the samples to air dry for two weeks. Several 1.5 g portions of the air-dried sediment were placed in 50 ml centrifuge tubes. Thirty ml of 0.5 M HCl were added to each tube. Each tube was then stoppered and placed on a shaker table and agitated for 12 hours at room temperature. After agitation, the tube was removed and centrifuged at 600 revolutions per minute (rpm) for three minutes. The supernatant was then analyzed for Cd, Zn, Hg, Pb, and As using the

atomic absorption spectophotometer.

Shell samples taken in Field Study II were processed in the following manner. The shell was rinsed with a 0.5 M NaOH solution to remove any residual tissue. It was then rinsed five times with distilled, deionized water and placed in 50 ml beakers. These beakers were dried at 103°C until a constant weight was obtained. After drying, the shell was stored in sealed containers. For analysis, 1.0 g of dry shell was placed in a 50 ml beaker and 6 ml of ultra pure HNO_3 (Ultrex, Baker Chemical Company, New Jersey) were added. This mixture was placed on a hot plate under an exhaust hood and heated until the liquid evaporated. Once the beaker had cooled, another 6 ml of ultra pure HNO3 was added and the beaker was covered with a watch glass and heated slowly until a reflux condition was reached. Refluxing was allowed to continue until the solution had evaporated. The watch glass was then rinsed into the beaker with 2 ml of 0.5 percent ultra pure HNO3. This liquid was poured into a graduated tube. The beaker was rinsed five times, each time with 1 ml portions of ultra pure HNO3 which were also poured into the graduated tube. An additional 3 ml of 0.5 percent ultra pure HNO_3 was then added to the tube, bringing the total volume in the tube to 10 ml. The tube was then sealed with parafilm and the sample was analyzed within one week for Cd and Zn.

IV. RESULTS

The results of the four major areas of this research are covered in individual sections of this chapter. The first section contains data from the three field studies. The second section contains the results of the two tank studies. The third section contains data from the analysis of the COD and BOD of both the alginate and scrap. The fourth section contains data obtained from thehCd adsorption study.

Field Studies

These studies are presented in the sequence in which they were undertaked. For each field study, the sites are first characterized by weather, tidal, and water quality data. This site characterization is followed by a description of the appearance of the crab scrap. In Field Study II, the concentrations of selected metals present in the water, bottom sediment, and scrap shells are also given.

Field Study I

Characterization of Sites

The characteristics and water quality data for each of the three sites used in this study can be found in Table II. These data indicate that the water at the three sites contained only trace amounts of total organic carbon, selected

	SI	ite A		Site B			Site C	
Date Sampled	5/2/82	5/15/82	5/1/82	5/2/82	5/15/81	5/1/82	5/2/82	5/15/82
Time Sampled	0011	1630	1550	1310	1945	1950	1430	1830
Sky Conditions	Cldy	Clear	Clear	Rain	Clear	Clear	Stmy	Clear
Seas	Chpy	Сһру	Chpy	Calm	Calm	Calm	Calm	Calm
Time of the Tide, EST								
High	0540	1528	1714	1813	1528	1714	1813	1528
Low	1203	2127	1102	1203	2127	2323	1203	2117
Depth (m)	3.0	5.2	3.2	2.8	2.5	2.5	1.5	2.0
Velocity (m/sec)	ì	7.8	ł	t	9.6	I	ł	6.0
Salinity (ppt)	20.0	18.6	19.2	13,9	14.2	12.0	10.8	10.6
Secchi (m)	ي. ت	3.0	1.2	1.2	1.0	C. 8	0.5	0.5
Surface pH	8.2	8.3	8.2	8.2	8.4	8.2	8.0	7.2
Water Temp. (^O C)	15	18	18	16	18	17	18	22
D.O. (mg/L)	9.0	7.0	9.3	7.9	8.2	8.8	7.6	7.0

TABLE II. CHARACTERISTICS OF FIELD SITES A, B, AND C

Table II. Continued

<0.002 0.041 12.2 8.8 <50 6.2 4. 70 4 7 5 <0.002 Site C 0.037 Muck <0.5 14.5 6.0 <50 5.8 \$ ∇ v <0.002 0.036 11.6 <0.5 7.2 0.3 <50 4~ 5 $\overline{\mathbf{v}}$ <0.002 0.010 <0.5 12.2 0.2 <50 4.5 7 7 7 7 Site B <0.002 0.008 <0.5 Mud 0.4 <50 <50 01> 3.1 4 $\overline{\nabla}$ $\overline{\nabla}$ <0.002 0.013 <0.5 11.5 2.2 <50 3.8 7 $\overline{\mathbf{v}}$ $\overline{\nabla}$ <0.002 <0.005 11.9 <0.5 2.0 Site A 3.8 <50 20 7 5 ∇ Sand <0.005 <0.002 <0.5 <50 2.3 50 3.7 44 $\overline{\nabla}$ V i $NO_2^- + NO_3^-$ (mg/L as N) Organic N (mg/L as N) Ammonia (mg/L as N) Alka. (mg/L as N) (mg/l.) (mg/L) Cadmium (mg/L) Arsenic (mg/L) Mercury (mg/L) Iurbidity (NTU) Bottom Type T0C (mg/L) Lead Zinc Metals

metals, and nitrogen containing compounds. The concentrations of TOC found at the sites ranged from 10 to 14.5 mg/L. The concentrations of ammonia, organic nitrogen, $NO_2^- + NO_3^$ were all below the detectable limits of 1 mg/L for ammonia and $NO_2^- + NO_3^-$ and 4 mg/L for organic nitrogen. (The concentrations of Pb, As, Hg, and Cd were less than 50 mg/L; less than 1.5 mg/L; less than 6.3 mg/L; less than 0.042 mg/L, respectively.) These data indicate that the water at the three sites was of good quality. These data also show that water depth and current velocity were variable.

Appearance of Scrap

The initial (after 24 hours) inspection at Site A was impractical due to adverse weather conditions.

At Site B, after 24 hours of exposure, three of the five uncoated scrap balls had separated into small pieces, while two were intact. Two of the five coated scrap balls had separated into halves which were still well compressed. Three were intact.

At Site C, after 24 hours of exposure, all of the uncoated scrap balls were still intact. Two of the coated scrap balls were intact, while two had separated into halves and one was missing.

All three sites were inspected 13 days after the initial (24 hours) inspection. At Site A and Site B the con-

tainment devices could not be located. The control containment device which had been placed at Site B was found 50 yards from its original position and had become entangled in sunken wreckage. This seemed to indicate that strong tidal currents may have relocated the other containment devices. The containment devices were found to be in place at Site C. No scrap was found in either device and the bottom of both devices had become filled with a two-inch layer of muck.

Field Study II

Characterization of Sites

The characteristics and water quality data for each of the three sites used in this study can be found in Table III. These data indicate that the water at the three sites contained trace amounts of total organic carbon, selected metals, and nitrogen-containing compounds. The concentrations of TOC at the sites were consistently below the level of 10 mg/L. The concentrations of organic nitrogen, ammonia, and $NO_2^- + NO_3^-$ were all below detectable limits. These data indicate that the water at the three sites was of good quality. The site depths at the sites ranged from a low of 4.0m at Site D to a high of 10.5m at Site F. The salinity at each of the sites remained nearly constant at 14 ppt. Figures 14, 15, 16, 17, 18, and 19 show that temperature and dissolved oxygen varied with depth at the three sites. The

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TABLE

6/27/82 1040 P.Cldy Calm 1642 1024 1024 10.0 Fig.20 7.8 14.2 1.2 0.9 *4 49.7 10 3.3 ŗ Site F Muck 1636 2300 10,5 Fig.19 7,5 7,5 14,0 1.5 1.5 *4 *2 6/5/82 1830 P.Cldy Calm 50.2 10 1.9 ۲. 6/27/82 1145 P.Cldy Calm 1642 1024 5.0 Fig.18 8.0 14.3 2.2 2.2 49.3 10 3.7 ~ Site E Muck 6/5/82 1730 P.Cldy Calm 1636 2300 Fig.17 7.5 114.0 1.0 2.2 2.2 50.4 10 1.7 6/27/82 1230 Cldy Sl.Chop 1642 1024 4.0 Fig.16 8.3 13.8 13.8 13.8 50.0 10 3.2 Site D Muck 1636 4.5 Fig.15 7.7 14.0 1.0 0.9 6/5/82 1615 P.Cldy Calm 51.8 10 2.7 Date Sampled Time Sampled Sky Conditions Seas Time of Tides High Low Depth (m) Temperature Dissolved Oxygen PH Salinity (ppt) Salinity (ppt) Secchi (m) Velocity (m/sec) Organic N (mg/L as N) Anmonia (mg/L as N) $NO_{2}^{-} + NO_{3}^{-}$ (mg/L as N) Alka. (mg/L as CaCO $_3$ TOC (mg/L) Turbidity (NTU) Bottom Type

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Figure 15. Water temperature and dissolved oxygen variations with depth at Site D at 1615 hours on 5 June 1982.



Figure 16. Water temperature and dissolved oxygen variations with depth at Site D at 1230 hours on 27 June 1982.



Figure 17. Water temperature and dissolved oxygen variations with depth at Site E at 1730 hours on 5 June 1982.



Figure 18. Water temperature and dissolved oxygen variations with depth at Site E at 1145 hours on 27 June 1982.



Figure 19. Water temperature and dissolved oxygen variations with depth at Site F at 1820 hours on 5 June 1982.



Figure 20. Water temperature and dissolved oxygen variations with depth at Site F at 1040 hours on 27 June 1982.

most drastic variation in D.O. occurred on 25 June 1982 at Site D. At a depth of 0.5 m below the surface, the D.O. was 7.8 mg/U while at a depth of 4.5 m, the D.O. was 1.4 mg/L. Sites E and F showed similar variations on 25 June 1982.

Appearance of the Scrap

Following 24 hours of exposure to the marine environment at the three sites, all of the scrap balls, both coated and uncoated, had disintergrated. It appeared as though only 50 percent of the tissue remained in the containment devices. All of the shell material seemed to remain in the devices. After ten days of exposure, the devices at all three sites contained only shell material.

The concentrations of selected metals can be found in Table IV. Figure 21, shows the amounts of Cd and Zn which were found in the water, sediment, and shell.

The concentrations of Zn in the sediment increased by less than ten percent at the three sites from 5 June 1982 to 15 June 1982. The concentrations of Cd in the sediment increased by 30 percent at Site D, by 55 percent at Site E, and showed no increase at Site F over the same time period.

The concentrations of Zn and Cd in the crab shell decreased over 50 percent at all sites over the ten day period of 5 June 1982 to 15 June 1982. The largest decrease was at Site F where the concentration of Zn was 1.5 mg/g.
	D, E, AND	F ON SELEC	TED DAYS IN	I JUNE OF 1	982				- -
	SITE D	6/5 SITE E	SITE F	SITE D	6/6 SITE E	SITE F	SITE D	6/15 <u>SITE E</u>	SITE F
WATER Pb(mg/L)	< 50	< 50	< 50	<50	<50	< 50	< 50	< 50	<50
As(mg/L)	<0.5	1.3	<0.5	<0.5	1.0	1.4	0.6	0.7	1.4
Hg(mg/L)	4.1	<0.2	<0.2	0.3	<0.2	<0.2	<0.2	<0.2	<0.2
Cd(mg/L)	<0.002	<0,002	0.003	0.005	0.005	0.006	<0.002	<0,002	0.004
Zn(mg/L)	0.010	0.005	0.005	0.014	0.007	0.076	0.015	0.003	0.010
SEDIMENT									
(6/6m)dq	0.0013	0.0016	0.0017	ŧ	ı	ı	0.0013	0.0017	0.0016
As(mg/g)	0.152	0.170	0.230	1	ı		0.146	0.223	0.242
Hg(mg/g)	0.004	0,007	0.006	ł	I	ı	0.003	0.004	0.006
Cd(mg/g)	0.018	0.024	0.029	I	ſ	1	0.030	0.053	0.027
Zn(mg/g)	3.63	4.36	4.52	ł	·	ı	3.95	4.62	4.86
SHELL									
Cd(mg/g)	0.009	0,009	0.101	0.009	0.007	0,009	0.005	0.005	0.007
Zn(mg/g)	2.6	2.4	2.3	2.1	2.2	2.5	1.2	0.8	0.8

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TABLE IV. THE CONCENTRATIONS OF VARIOUS METALS FOUND IN THE WATER, SEDIMENT AND SHELL AT SITES



Figure 21. Concentrations of Cd and Zn found in the water, sediment and shell at Sites D, E, and F.

The concentration of Cd in the crab shell also showed a definite, but not as drastic a decrease. This decrease ranged from approximately 25 percent at Site F to 50 percent at Site E.

The concentration of Zn in the water at the three sites remained constant at 0.2 mg/L. The concentration of Cd at each site increased by at least 50 percent from 5 June 1982 to 6 June 1982, but then decreased back to the levels measured on 5 June by 15 June 1982. The maximum concentration of Cd measured in the water was 0.005 mg/L.

Field Study III

Characteristics of Sites

The three sites used in this study are the same as those used in Field Study II. The site characteristics and water quality data may be found in Table III.

Appearance of Scrap

After two days of exposure, all of the scrap balls at each site had disintegrated and approximately 50 percent of the tissue remained. The unground, uncompacted scrap at each site was still intact with 75 percent of the tissue remaining after two days. At the end of four days of exposure, only 30 percent of the tissue from the scrap balls remained. Whereas, after four days, approximately 50 percent of the

tissue remained on the unground shells at each site and the integrity of the shell material seemed to have been diminished. After six days, no tissue from the scrap balls remained and only trace amounts of tissue remianed on the unground crab shells at each site. The unground shell material apopeared "pitted" as if something had been removed. When finger pressure was gently applied to the shell, it crumbled easily.

Tank Studies

<u>Tank S</u>tudy I

In this study three different forms of crab scrap were immersed in tanks of aerated, dechlorinated tap water. Tank A contained loose scrap, Tank B contained compacted scrap, and Tank C contained compacted, coated scrap. Both analytical and sensory observations of change were made.

Sensory Observations

The appearance of the scrap, the odor of the water, and the color and appearance of the water were the sensory observations made. These observations were made daily and a detailed listing can be found in Table V.

In comparing the three methods of scrap preparation through sensory observations, the following information was

TABLE V. SENSORY OBSERVATION MADE DURING TANK STUDY I.

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. 		COLO	R AND APPEARANCE OF THE WATER		
	TANK A		TANK B		TANK C
Day O	The water became turbid upon addition of the loose scrap	Day D	The water was very clear after addition of the compacted scrap.	Day D	The water remained clear after addition of the scrap.
Ddy 1	Clarity of the water had de- creased significantly.	Day 1	Water clarity decreased rapidly.	Day 1	The water was slightly turbid.
ilay 2	The water within one inch of the scrap had taken on an orange- yellow hue.	DAY 2	The water was translucent.	Day 2 - 3	Water clarity was moderate.
luy 3	The bottom two inches of water was orange-yellow.	Ddy 3 • 4	The water clarity continued to decrease. An orange-yellow color had appeared.	Day 4 - 24	The water was translucent.
Day 4 - 9	The water was extremely turbid throughout the tank, but the color had disappeared.	Day 5 - 9	The water was still translucent, but the color had disappeared.		
Uay 10	The turbidity agglomerated and began to settle. Water clarity had increased markedly.	Day 10 - 17	Visibility was increasing daily.	Day 25 - 34 - 24	Water clarity was increasing.
[] [] [] [] [] [] [] [] [] [] [] [] [] [] [] [The water appeared very clear.			dE YBU	No odor was detected,

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	TANK C	etected. Day D No odor was detected.	,		r was noticed.	1 Day 4 Only a slight odor was detected.	- 24 1 to decrease.	tected. Day 25 The odor was slight, no offensiv
GDOR OF THE WATE	TANK B	Day 0 No odor was d			Day 3 Offensive ado	Day 4 Odor decreased	Day 5 Odor continued - 9	Day 10 Nu odor was de
	IANK A	No detectable odor was noticed.	Slightly affensive ador was detected.	Odor had become very offensive.	Putrid odor was noted. Began to swell like 'natural' gas.	údor decreased,	Udor continued to decrease.	No odor detected.
		Day 0	Day l	0ay 2	Day J	Day 4	ι 9 10 -	1137 10 - 17

Day 35 No odor was detected.

0 The compacted scrap block boke Day 0 The compacted scrap block boke Day 0 The compacted scrap block boke 0 The main surface. In bit is stant, but each haif Scrap block was placed in the surface. 1 Nost of the scrap run in the surface. Day 1 The compacted scrap block boke Day 0 The compacted scrap floated. 1 Most of the scrap remained on the surface. Day 1 Some small pieces Day 1 The scrap block was placed in the some scraption. 1 Most of the scrap run in the currents created bit most of the scrap run in the currents created by the areation. Day 0 The scrapted to be some-wing the scraption in equation the scraption. 1 Most of the scrap run of the last. A few swim- Day 1 The scrapted to be some-wing the scrapted to be some-wing the areation. 2 All scrapted in the scrapted to the scrapted to be some-wing the areation. Day the areation. Day the areation. 3 All scrapted in the scrapted to be some-wing the areation. Day 1 The turrents created to be some-wing the areation. 3 All scrapted in the scrapted to be some-wing the areation. Day to be the scrapted to be some-wing the areation. Day to be the scrapted to be some-wing the areation. 3 All scrapted and the two scrapte		TANK		APPEARANCE OF SCRAP IANK B		TANK C
 Most of the scrap remained on the Day 1 Some small pieces had broken away. Day 1 The block remained in one piece. The but most of the scrap remained in -24 but most of the scrap ter was noted. 3 All scrap had sunk. Nuthing the nast inter was noted. 17 The tank was cleaned and the two Day 25 All visible surfaces of the block were covered with biological growth. The tank was cleaned and the two Day 25 but the block had split in half. One second mode the meat remaining on the shells. 17 The tank was cleaned and the meat remaining on the shells. 18 All scrap had surfaces of the block remained in the shells. 19 The tank was cleaned and the meat remaining on the shells. 10 All scrap had surfaces of the block remained in the shells. 11 The tank was cleaned and the two Day 25 but for the other maintained to the state of the block had split in half. One second mode the other maintained the shells. 11 The tank was cleaned and the two Day 34 the block remained to the other maintained to the shells. 	I G	file majority of the scrap sunk innuediately and only a few small swimmerets floated on the surface.	Day 0	The compacted scrap block broke in half as it sank, but each half remained intact. Some small pieces of scrap floated.	Day 0	The compacted, alginate- coated scrap block was placed in the tank. It maintained its structural integrity, but appeared to be some- what buoyant in the currents created by the availon.
3 All scrap had sunk. Nothing floated. 17 The tank was cleaned and the two Bay 25 All visible surfaces of the block were scrap was examined. Only shell pay 17 The tank was cleaned and the two Bay 25 All visible surfaces of the block were scrap was examined. Only shell pay 18 talves examined. There was very - 32 covered with biological growth. 18 talves examined. Day 33 The biological growth. 19 the tank mas cleaned and the two Bay 25 All visible surfaces of the block were active was examined. Only shell pay 17 the biological growth. 19 talves examined. There was very - 32 covered with biological growth. 19 the tother maintened its shape and had begun to single off. 10 and the other maintened its shape and had begun to begun floating. Gas may lave been traped prove been traped provement the algivate coating. 19 and apparent? 19 and apparent? 19 and so cleaned. The start the tank was cleaned. The start the talvater to the start to the start the talvater. 10 and only shell start the talvater to the start the talvater. 10 and only shell start the talvater to the start to the start the talvater to the start.	_	Most of the scrap remained on the bottom of the tank. A few swim-merets were still floating.	Day - 16	Scame small pieces had broken away, but most of the scrap remained in two larye pieces. No floating mat- ter was noted.	Day } - 24	The block remained in one piece.
17 The tank was cleaned and the Day 17 The tank was cleaned and the two Day 25 All visible surfaces of the block were scrapt was examined. Duly shell talves examined. There was very -32 covered with biological growth. Teurained. Duly shell Title meat remaining on the shells. Day 33 The biological growth had begun to slough off. Day 34 The block had split in half. One section for the other maintained its shape and had begun to slough off. Day 34 The block had split in half. One section for the other maintained its shape and had begun floxing. Gas may Pave been traped beyon floxing. Floxing the scrap was examined beyon floxing.	~	All scrap had sunk. Nuthing floated.				
Day 34The block had split in half. One section had broken up completely, while tion had broken up completely, while the other maintained its shape and had begun floating. Gas may have been tra ped beneath the algivate coating.Day 35The scrap sunk. The gas had apparently been released from the block. After ti tank was cleaned, the scrap was examina and colly shell remained.	2	The tank was clraned and the scrap was examined. Only shell remained.	Day 17	The tank was cleaned and the two halves examined. There was very little meat remaining on the shells.	Day 25 - 32 Day 33	All visible surfaces of the block were covered with biological growth. The biological growth had begun to slough off.
Day 35 The scrap sunk. The gas had apparent) been released from the block. After th tank was cleaned, the scrap was examin- and only shell remained.					Day 34	The block had split in half. One sec- tion had broken up completely, while the other maintained its shape and had begun floating. Gas may have been trap ped beneath the algimate coating.
					Day 35	The scrap sunk. The gas had apparently been released from the block. After th tank was cleaned, the scrap was examine and only shell remained.

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TABLE V. CONTINUED.

obtained. Water quality, in the forms of odor, clarity, and color of the water, was more severely impacted in Tank A than in Tank B and more severely in Tank B than in Tank C.

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The odor in Tank A was first detected on Day 1, reached its peak on Day 3, and was undetectable after Day 10. In Tank B the odor was first noticed on Day 3, also reached its peak on Day 3, and was gone by Day 10. The peak odor in Tank A was much more offensive than the peak odor in Tank B. Tank C exhibited only a very mild odor from Day 4 to Day 34. This odor was never offensive.

The clarity of the water in Tank A began decreasing immediately after addition of the scrap. This decreased clarity continued until Day 10, when particles in the water column began to agglomerate and settle out. From Day 10 to Day 17, the water appeared to be very clear. On Day 2 and 3, in Tank A, the water around the scrap was an orangeyellow color. In Tank B, the water remained clear after the addition of the scrap. The water clarity began decreasing on Day 1 and continued to decrease until Day 4. On Day 3 and 4, an orange-yellow color was present around the scrap. After Day 9, the water clarity began to improve. At no time was the water clarity as poor in Tank B as it was in Tank A. Water clarity in Tank C began decreasing on Day 1, but was not translucent until Day 4. The water remained translucent until Day 24 and then began to clear.

The water in Tank C was always clearer than the water in Tanks A and B.

Analytical Observations

Analytical changes in the water quality of each tank were monitored daily for the first six days of this study. The parameters analyzed were water temperature, dissolved oxygen, turbidity, BOD_5 , TOC, pH, and NH_3 . Figures 22, 23, 24, and 25 present NH_3 , turbidity, TOC, and BOD_5 data, respectively, for the three tanks. The values for pH, D.O., and temperature remained almost constant in all three tanks over the first six days.

<u>NH</u>3

The NH_3 concentrations in each of the tanks followed the same general trend; that is, it increased slowly for the first three days, increased rapidly from day three to day five, and then leveled off or decreased slightly on day six. On all days, the NH_3 concentrations found in Tank A were approximately twice those found in Tank B and four times those found in Tank C. The initial NH_3 concentration in the water used in the three tanks was less than 1.0 mg/L. The maximum NH_3 concentrations measured were 33 mg/L for Tank A, 19 mg/L for Tank B, and 6.8 mg/L for Tank C.



Figure 22. Daily variations in the concentration of NH₃ in the water in Tanks A, B, and C during the first³six days of Tank Study I.

Turbidity

The turbidity in each of the tanks was found to follow the same trend through day four. It increased from day zero to day two, decreased from day two to day three, increased again from day three to day four. After day four, the turbidity continued to increase in Tank A and decreased or leveled off in Tanks B and C. The turbidity in Tank A was almost twice that of Tank B and four times that of Tank C, as was similarly noted for the NH₃ concentrations. The initial turbidity in the water used in the three tanks was less than 1.0 NTU. The maximum turbidities measured were 33 NTU for Tank A, 14.5 NTU for Tank B, and 6.6 NTU for Tank C.

TOC

The TOC concentrations in all three tanks followed similar trends. TOC levels sharply increased on day one, sharply decreased on days two and three, and then changed relatively little after day three. The only deviation from this trend occurred in Tank B on day five and was so drastic that it may have been due to an erroneous reading. The initial concentration of TOC in the water used in the three tanks was less than 1.0 mg/L. Tha maximum TOC concentrations measured were 41.5 mg/L for Tank A, 19.4 mg/L for Tank B, and 8.8 mg/L for Tank C.



Figure 23. Daily variations in the turbidity of the water in Tanks A, B, and C during the first six days of Tank Study I.



Figure 24. Daily variations in the concentration of TOC in the water in Tanks A, B, and C during the first six days of Tank Study I.

BODE

Tank A and Tank B each exhibited the same trend in BOD_5 changes with the values for Tank A being much greater than those for Tank B. The BOD_5 level of Tank C did not change. It remained less than 12 mg/L. The initial concentration of BOD_5 in the water used in the three tanks was less than 12 mg/L. The maximum BOD_5 values were 130 mg/L for Tank A and 36 mg/L for Tank B.

<u>Tank Study II</u>

In this study, coated scrap balls were immersed in tanks simulating four different environments. These environments, were aerated saline water with no sediment in Tank D, aerated saline water with sediment in Tank E, nonaerated saline water with sediment in Tank F, and nonaerated saline water with no sediment in Tank G. Both sensory and anlytical observations of change with time were made.

Sensory Observations

The appearance of the scrap, the odor of the water, the amount and type of floating matter present, the presence of biological growth, and the color and visual appearance of the water were the sensory observations made. These observations were made on days 0, 1, 2, 3, 5, 7, 9, 11, 13,



Figure 25. Daily variations in the concentration of BOD_ in the water in Tanks A, B, and C during the first six dags of Tank Study I.

16, 19, 21, 29, and 36. Table VI provides a detailed listing of these sensory observations.

In comparing the four different marine environments, it was observed that the two aerated environments were impacted similarly by the addition of crab scrap. The two nonaerated environments were impacted in very different ways.

Appearance of Scrap

The alginate coatings had sloughed off the scrap in each of the four tanks by Hour 4. By Day I, all the scrap had disassociated, but it was remaining in a distinct mound in each tank. This distinct mound of scrap remained in Tanks D and E for the duration of the experiment. The only changes being a reduction in size with time and the formation of a mat of biological material over the mound. The mounds in Tanks F and G both began producing gas which carried scrap to the water's surface and caused it to float and then later, to sink. This movement of scrap through the water column caused the scrap to be dispersed throughout the tanks. In Tank F, all the scrap had fallen out of the water column by Day 11 and no floating scrap was seen from Day 11 to Day 36. Scrap continued to float in Tank G up through Day 36.

II
STUDY
TANK
DURING
MADE
OBSERVATIONS
SENSORY
٧I.
TABLE

			COLOR AND APPEARANCI	OF THE	ATER		
	TANK 0		TANK E		TANK F		IANK G
(ye)	The water was a murchy yellow- green and was no hunger trans- parent. A foom had beyon to form on the water's surface.	Dey I	The water was murky and yellow- green and the scrap was not visible.	l yed	The water was turbid but still transparent	Day 1 8 2	The water had stratified. The upper water was clear while the lower 10 m of water were very turbid.
Ulay 2	The scrap was visible and the from had decreased.	Day 2	foam had beyun appearing on the water's surface. The water had cleared slightly.	Day 2	The surface water was still transparent, but a water layer 4 cm in depth over the seciment had turned very black.		
Uay 3	The water cleared considerably. The scrap was visible. Small amounts of foam were nuted.	E Yall	foam had filled the entire area dowe the water approximately 10 cm, and had seeped out of the lank. Turbidity was decreasing.	Day 3	The black zone increased to a depth of 5 cm.	Dey 3	Dark waler was noticed around the edges of the scrap heap.
Nay 5. 74.9	The turbidity was decreasing No fuam was present.	Clay 5	fuam was escaping from the tank.	Day S	Black zone was 8 cm deep	0ay 5 8 7	The bottom 10 cm of water were turbid and black.
		Day 7	The foam had decreased markedly.	Day 7	The turbidity had increased.		The supernatant water was clear.
		Day 9	Water clarity was increasing. The foam had decreased further.	Day 9	The color stratification had begun to disperse.	Day 9	The water had beyun to destratify.
Hay II	The tank was again transparent. Foam was not present	Day 11. 13. 5 16	. The foam was completely yone and the water was clearing.	Day 11	Water color stratification was not detectable.	Day 11	The water was very tur- bid. No turbidity stratification was noted.
() ay 13 6 16	The clarity of the water was furproving.			0ay 13. 16. 5 19	The turbidity was steadily in- creasing.	Day 13. 16, 19, 22, 4 29	. The turbidity was la- creasing sitahtly.
22 29	. Water was completely clear.	Day 19	The water was completely clear.				
8 36		0 ₄ y 22 29 4 36	The water remained clear.	Bay 22	The water had turned reddish- brown.		
				Day 29 1 36	The water was turbid but clear- ing. It was reddish-brown.	Day 36	The turbidity appeared to have decreased.

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	I AMK D		IANK E SCRAM APPEA	IRANCE	IANK F	TANK G
Hour 4	The alginate coarting had stoughed off.	Hour 4	The alginate coating had No.	10r 4	The alginate coating had Hour 4 sloughed off.	The coating had sloughed
Day l	The scrap was not visible.	Day 1	The scrap was not visible. Ba	-	The scrap had totally disas- Day P the scrap had totally disas- Day P one mound. Gas was occasion- ally released from the scrap to the surface.	The scrap was in a mound where the scrap ball had been and swall sections of the coating were present.
2 YEQ	fhe scrap completely dis- assuciated.	Day 2	The scrap was totally disas- Day sociated but the majority of scrap remained in one around. A tew particles were suspended in the water column.		The scrap mound and the sedi- Day 2 Ment both released large bub- bles of gas. Some scrap and which had formed at the water's	Small pieces of floating scrap were noticed, Black color appeared in the
Uay 3, 5, 7 8 9	The scrap rematined in a moun but the size of the mound way slowly decreasing. Only she and biolugical mat remained.	d.Day 3, 5, 5 7 5 9 11	The scrap remained in a mound but the size of the mound was Day sluwly decreasing.	 	surface. When the scrap reached the wat-Day 5 A er's surface, the gas escaped 7	water around the scrap mound. The scrap was moving verti- cally through the water
		Day 11	All tissue appeared to be gone. Unly shell and a biological mat remained.		and the scrap began to fall. but it did not return to the Sediment. A band of suspended	column.
Day 13, 16, 19,	the shell remained in a wound covered by a mat of	0ay 13, 16, 22,	The shell remained in a mound covered by a mat of new bio-		tween the turbid and clear lay- ers of water.	
1 , 2, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2,	utulugical material.	29 8 36	loyical material. Day	 \	The scrap was moving vertically through the water column.	
			Day	 	Most of the scrap remained sus- Day 9 pended somewhere in the water column.	Larye amounts of floating Scrap were present, with Strands of Scrap Which hund
			Day 16 22 36	29, 19, 5,	No scrap was floating or suspen- ded in the water column, 0ay 11, 13, 19, 22, 29, 8 36	from the water's surface. White biological mats were floating on the water's sur- face. Floating scrap was present.

. [FLOATING	MATTER			
: :			TANK E		TANK F		TANK G
1, 2, 0 2, 5, 1 2, 5, 5, 1 2, 5, 1, 5,	No Floating scrap delected.	1. 2. 1. 2.	No floating scrap wis abserved,	0ay 8 2	Small particles of scrap were floating on the surface,	Day 1	Nu floating material present.
		•		Day 3	Scun formed on the surface and contained trapped gases and scrap.	Day 2, 3 5 5	Small pieces of scrap Were floating.
				Day 5 6 7	Scum and scrap were floating on the water's surface.	Day 7	Large amounts of float-
		Day 9	Small bits of floating scrap were detected.	Day 9	Large amounts of scrap were floating on the success	Day 9	Strands of stran were
(T Yed	The hat of new biological water- ial which had formed over the straten unound becan floaten unou	II Yed	Nu fluating scraws were detected.	Day 11	While biological mats were found on the water's configuration		hanging down from the floating scrap.
	a gus budble became trapped he- neath it.				was floating.	Day 11 13, 16 10 ± 23	Scum and scrap were Dresent on the water's
61 45 13 8 16	The biological mat was floating.	61 y 13 8 16	A floatiny mat of shell and bio- Dogical matter was observed	Day 13 16 10	No floating scrap. The area of	77 B	surrace. While biolog- fcal material had formed on the water's surface.
Day 19	The blological mat sunk.	Day 19	The floating mat had sunk.	22, 29 8, 36	rue stum layer decreased. White biological mats floated on the water's surface.	Bdy 29 6 36	Floating mats of mixed scrap and biological material had begun to
liay 22 29 6 36	No floating material detected.	Cay 22 29 6 36	No floating meticr detected.				

	(Attr D		810L061CAt +	SROWTH			
			<u>IANK E</u>		TANK F		TANK C
luy u	Nu attached brokugreak yruwrh delected.	6ay 0. 1 b 2	No attached biological growth was detected.	Day 0 1,2,3	No attached bialogical growth detectable.	Day 0	Nu biological growth was
لم بردن	Bioloyical growth was noted an tank walls.			5,789			
£ you	White biological growth was noted arnund the edges of the scrap.	Day J	A small amount of biological growth was moted on the walls of the tank.				·
fiay S	A must of biological growth had formed over the scrup and tank bottom.	Û≜y 5	Biological growth on the tank walls had increased slightly.				
1 4rd 6 1	The must continued to increase in size.	0ay 7	A biological mat had formed over the sediment and scrap,				
Uuy 11	ihe wal began floating	Day 11 4 1 3	The biological growth on the tank wells was fucreasing.	Cl VeQ	The first biological growth was detected. White biological mats appeared on water's surface.	Day 11	White wats of biological material had formed on the ustor's confised
(lay 1)	Biological gorwth had reestab- lished on the shell.			Day 13	The area of the white blological mats increased	Day 13	White mats of biological
18 16 19 522 19 522	Biological growth on shell con- tinued to increase.	Day le	The biulogical growth on the walls of the tank had increased signifi- cantly.	Døy 16	Green biological material was detected on the tank walls.	22 8 29	material were present at the water's surface.
45 Yof	the density of the biological muterial on the walls of the tank had beyon decreasing.	0ay 10 22, 29 5 36	The biological growth on the tank walls was decreasing.	Day 19	Green biological material had formed long streaks on the walls of the tank. Bruwn streaks had also formed and the white mats were still on the water's surface.		
de yes	Wery little biulogical material on the walls of the tank. But- tam mat of biological material had also decreased.			04y 22 29 6 36	The walls were completely covered with red, yreen, and brown bio- Jogical muterial.	Day 36	A few green and brown streaks had furmed on the tank walls. White biological material was present at the water's surface.

:			OBOR OF THE WAY	8			
	LANK D		TAUK E		TANK F		IANK G
Vay I	A tishy odor was detected.	Day 1	A fishy odor was detected.	Day 1	A fishy odor was detected	04 1	A fishy odor was lietec-
Day 2	The fishy odor had decreased.	Day 2	The odor increased.	Day 2	A slight sulfur odor was de- lected.	7 0	190 He .
l yau	the udor had increased but re- spin-bed that of annionia.	Day 3	A strong ammunia odor was detected The fishy odor was gone.	Day 3	The sulfur odor had increased.	0ay 3	The fishly odor had dis- appeared and a sulfur
buy 5	The amounta odor increased.	Day S	The ammunia odor increased,	Day 5	A strong sulfur ador was detec- table.	Day 5	ador uegan to develop. A strong sulfur odor was
Nay 7	The annunta udor was very strong.	Day 7	The ammonia odor was very strumy.	Day 7 9 8 11	The sulfur odor had become stronger.	11. 13 16. 19	derectante.
د روال 11 ه 11 13	The aumunia odor wás Jerreasing narkedly.	0 4 4 0 11 A CO	The annunia udur had decreased. The annunta udur was decreasing.	04y]3 16 8 19	The sulfur odur was being re- placed by another equally strong odor.	77 9	
մել՝ են	The odor was completely gone.	91 Ård	The ammunia odor was completely yone.	Day 22	The odor was still strong but no longer suffur-like.		
04y 19 22, 29	No odor detected.	0ay 19 22, 29	lla ador wus detected.	0ay 29	The intensity of the odor in- creased.	Day 29	The odder had changed from sulfur to an odor
2 1		9		Day 36	The odur had decreased, but was still affensive		similar to that of sewage,
						0ay 36	A strong ulfur odor was ogatn detectable.

Odor of the Water

In Tanks D and E, a fishy odor was first detected which later developed into an ammonia odor. This odor peaked by Day 7 and then decreased until there was no detectable odor after Day 16. In Tanks! F and G, the initial odor was also a fishy odor, but by Day 3, the odor had changed to a distinct sulfur odor. In Tank F, the sulfur odor persisted until Day 13 when another equally strong odor replaced it. This odor remained until Day 36. In Tank G, the sulfur odor remained until Day 29 when it was replaced by another strong odor. The sulfur odor returned by Day 36.

<u>Floating</u> Matter

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The only floating matter observed in Tank D was the biological mat which had covered the scrap mound. On Day 11, a gas bubble became trapped beneath it and caused it to float until Day 19. In Tank E, small bits of floating scrap were seen on Day 9 and on Days 13 and 16, a floating mat of shell and biological matter was observed.

In Tank F, small particles of floating scrap were observed on Days 1 and 2. By Day 3, a scum had formed over the water's surface which contained trapped gases and scrap. The scum persisted and be Day 11 it contained white biological mats but no scrap. The scum and biological mats re-

mained through Day 36.

In Tank G, small particles of floating scrap were observed on Days 2, 3, and 5. By Day 7, large amounts of scrap were floating and on Day 9, strands of scrap hanging down from the water's surface had formed. A scum layer and mat of white biological matter had formed on the water's surface by Day 11 and these layers persisted through Day 36.

Biological Growth

The first biological growth to appear in Tanks D and E, on Day 2 and 3, respectively, was on the walls of the tanks. This was followed by the formation of biological mats over the scrap mounds. White biological growth was seen in both tanks.

In Tanks F and G, no biological growth was visible until Day 11, when white biological mats began to form on the water's surface in both tanks. Green, brown, and red streaks of biological growth began to form on the walls of Tank F on Day 16 and by Day 22, the tank walls were completely covered with biological material. These streaks were first seen in Tank G on Day 36.

Color and Appearance of the Water

The water in Tanks D and E turned a murky yellow-green by Day 1. A foam appeared on the water's surface in Tank D

on Day 1 and traces of the foam remained until Day 5. In Tank E, the foam first appeared on Day 2 and by Day 3, a 6 cm layer had formed above the water's surface. By Day 11, the foam had disappeared. The water clarity in both tanks had begun improving by Day 3 and by Day 19, the water was as clear as before the scrap was added.

In Tanks F and G, the water remained clear near the surface, but became black and turbid around the scrap. The water in both tanks remained stratified with respect to turbidity until Day 9. After destratification was complete, on Day 11, the water in both tanks became more turbid, with the water in Tank F becoming reddish-brown by Day 22.

Analytical Observations

Analytical changes in the water quality of each tank were noted on day 0, 1, 2, 3, 5, 7, 9, 11, 13, 16, 19, 22, 29, and 36. The parameters analyzed were pH, dissolved oxygen, temperature, turbidity, NH_3 , $NO_2^- + NO_3^-$, organic nitrogen, and TOC. These data, with the exception of temperature, are presented graphically in Figures 25 through 39.

Nitrogen Containing Compounds

Changes in the concentrations of the three different nitrogen forms in Tanks D, E, F, and G can be noted from Figures 26, 27, 28 and 29, respectively. These data are summarized in Figure 30.

In Tank D, the NH₃ concentration increased from less than 1 mg/L to a maximum of 62 mg/L by Day 7. It then decreased in an almost linear fashion to below the detectable concentration of 1 mg/L by Day 16. No NH₃ was detected after Day 16. Organic nitrogen was detected on only four of the sampling days: Days 2, 3, 11, and 13. It was never detected above 5 mg/L in Tank D. The NO₂ + NO₃ concentration varied somewhat erradically. A concentration of 2 mg/L was found on Day 2, then the concentration decreased to less than 1 mg/L and remained there until Day 9. From Day 9 to Day 36, the concentration of NO₂ + NO₃ alternately increased and decreased.

The nitrogen containing compounds in Tank E followed the same trends as did the nitrogen containing compounds in Tank D. Only minor differences were noticed.

In Tank F, the NH_3 concentration increased to 25 mg/L on Day 3 and then decreased to 5 mg/L by Day 5. After Day 5, the NH_3 concentration began increasing and continued to increase throughout the study, reaching a high value of



Figure 26. The variations in the concentrations of nitrogen containing compounds in the water in Tank D on the sampling days of Tank Study II.



Figure 27. The variations in the concentrations of nitrogen containing compounds in the water in Tank E on the sampling days of Tank Study II.



Figure 28. The variations in the concentrations of nitrogen containing compounds in the water in Tank F on the sampling days of Tank Study II.



Figure 29. The variations in the concentrations of nitrogen containing compounds in the water in Tank G on the sampling days of Tank Study II.





62 mg/L on Day 36, the last sampling date. Organic nitrogen was not detected until Day 2, when a concentration of 13 mg/L was found. The concentration then decreased in a linear manner, until it was again below the detectable level of 1 mg/L on Day 5. Organic nitrogen was not detected again until Day 11. After Day 11, the concentration remained between 1 and 10 mg/L on all sampling dates except Day 19, when it fell below 1 mg/L. The NO₂ + NO₃ concentration remained below the detectable level of 1 mg/L on all but three sampling dates, Days 7, 9, and 36. On these days, it remained below 10 mg/L.

The nitrogen containing compounds in Tank G followed the same trends as discussed above for Tank F.

TOC

The TOC concentrations for each tank can be found in Figures 31, 32, 33, and 34. In Tanks D and E, the TOC concentration increased to approximately 30 mg/L on Day 1, then decreased to approximately 25 mg/L on Day 2, and then increased slightly on Day 3. From Day 3 to Day 7, the TOC concentration remained constant and after Day 7, it began to steadily decrease. In Tanks F and G, the concentration of TOC increased sharply on Days 2 and 3, respectively. Following this sharp increase was a sharp decrease. After Day 7 the concentration of TOC varied erradically, increas-

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Figure 32. The variations in the concentrations of TOC in the water in Tank E on the sampling days of Tank Study II.



Figure 33. The variations in the concentration of TOC in the water in Tank F on the sampling days of Tank Study II.



Figure 34. The variations in the concentrations of TOC in the water in Tank G on the sampling days of Tank Study II.

ing and decreasing twice before reaching a level nearly equal to the initial TOC concentration.

pН

The pH data for Tanks D and E is presented in Figures 35 and 36, respectively. As noted from these figures, the pH data for these tanks are almost identical. They show a slight decrease from 7.9 to 7.4 on Day 1, followed by an increase to 8.2 by Day 5 and a leveling off.

The pH data for Tanks F and G can be found in Figures 36 and 37, respectively. The pH data for these tanks was almost identical also. These pH values decrease from 7.8 and 7.5, respectively, to values of 6.7 and 6.9 by Day 5. A very slow increasing trend was exhibited until Day 29, when the pH of the water in each tank dropped to almost 6.0. A return to pH values of approximately 7.0 was observed by Day 36.

The pH values in the aerated tanks ranged from 7.5 to 8.2, while the pH values in the nonaerated tanks ranged from 6.7 to 7.8.

Dissolved Oxygen

Figures 35 and 36 also provide the D.O. data for Tanks D and E, respectively. The D.O. concentration in each tank decreased from an initial value of 5.9 mg/L to a low of 4.5


Figure 35. The variations in the turbidity, pH, and the dissolved oxygen concentrations in the water in Tank D on the sampling days of Tank Study II.



Figure 36. The variations in the turbidity, pH, and the dissolved oxygen concentrations in the water in Tank E on the sampling days of Tank Study II.



Figure 37. The variations in the pH and the dissolved oxygen concentrations of the water in Tank F on the sampling days of Tank Study II.



Figure 38. The variations in the pH and the dissolved oxygen concentrations of the water in Tank G on the sampling days of Tank Study II.

mg/L on Day 1. After Day 1, the D.O. concentration began to increase until it reached a constant value of approximately 5.7 mg/L on Day 5.

Tanks F and G were both intended to be anaerobic tanks and the data in Figures 37 and 38 show that this was achieved. In Tank F, the D.O. concentration decreased to below detectable limits within one day, and remained there throughout the study. The D.O. level in Tank G decreased to about 0 mg/L within three days.

<u>Turbidity</u>

The turbidity data for Tank D and Tank E can be found in Figures 35 and 36, respectively. The turbidity in Tank D increased from 2 NTU to 22 NTU by Day 1, decreased to 6 NTU by Day 3, then increased to 13 NTU by Day 9. By Day 11, the turbidity had decreased to a value of 2 NTU and remained at or below 2 NTU until Day 36. The initial turbidity in Tank E was 17 NTU. The turbidity decreased to approximately 10 NTU by Day 2 and remained at this point until Day 13, when it decreased to 2 NTU. From Day 13 to Day 36, the turbidity remained at or below 2 NTU.

Figures 39 and 40 contain the turbidity data for Tanks F and G, respectively. Both tanks became stratified, with respect to turbidity, after about one day. They remained stratified, with the water near the surface of the tank



Figure 39. The variations in the turbidity of the water in Tank F on the sampling days of Tank Study II.



Figure 40. The variations in the turbidity of the water in Tank G on the sampling days of Tank Study II.

being less turbid than the water near the bottom of the tank, until Day 13. After destratification occurred, the turbidity increased markedly in Tank F, to a maximum of 60 NTU on Day 19 and then decreased to 24 NTU by Day 27. After Day 13, the turbidity in Tank G increased only slightly.

Oxygen Demand Study

BOD Analyses

Analysis of Scrap

An analysis of the scrap's BOD_5 was performed using both seawater and BOD dilution water as diluents. Table VII presents the data obtained when seawater was used in the analysis and Table VIII presents the data obtained when BOD dilution water was used. The average values and ranges of BOD_5 values for each diluent were similar. When seawater was used, the range of average values was 146 to 244 mg BOD_5 per g of scrap and, when dilution water was used, the range was 167 to 255 mg BOD_5 per g of scrap. It should be noted, however, that the BOD_5 exerted per gram of scrap decreased as the amount of scrap used in the analysis increased.

Analysis of Alginate

An analysis of the alginate's BOD₅ was also performed using both seawater and BOD dilution water as diluents.

257, 256, 219	244	146-244
225, 230, 219	225	
173, 171, 171	172	
144, 146, 148	146	
	257, 256, 219 225, 230, 219 173, 171, 171 144, 146, 148	257, 256, 219 244 225, 230, 219 225 173, 171, 171 172 144, 146, 148 146

Table VII. RESULTS OF THE BOD, ANALYSIS OF GROUND CRAB SCRAP USING SEAWATER AS THE TESTING MEDIUM

TABLE VIII.	RESULTS OF THE	BOD _c	ANALYSIS	0F	GROUND	CRAB	SCRAP	USING	BOD
	DILUTION WATER	AS TH	E TESTING	i me	EDIUM				

Amount of Scrap Analyzed (g)	mg_BOD ₅ /g_of_Scrap	<u>Average</u>	Range of <u>Avg. Values</u>
0.1	0.1 251, 228, 270 255	167-255	
	252, 252, 278		
0.4	161, 162, 141	167	
	180, 200, 169		

Table IX presents the data obtained when seawater was used in the analysis, and Table X presents the data obtained when BOD dilution water was used. The average values and ranges for the BOD data were relatively low. It appears that the BOD₅ of the material was less than 20 mg/g.

COD Analyses

Analysis of Scrap

The analysis of the scrap's COD was performed using deionized, distilled water as the diluent. Table XI presents the data obtained in this analysis. Note that the data ranged from a high of 416 mg of COD exerted per g of scrap to a low of 349 mg. The overall average was 390 mg.

Analysis of Alginate

The analysis of the alginate's COD was performed using deionized, distilled water as the dilution medium. Table XII presents the data obtained in this analysis. Note that the data ranged from 430 mg of COD exerted per g of alginate to 403 mg. The overall average was 417 mg.

Cadmium Uptake Study

This study involved the addition of differing amounts of crab shell to a 2.0 mg/L solution of Cd in seawater.

TABLE IX.	RESULTS OF THE BOD_	ANALYSIS OF	ALGINATE	USING S	SEAWATER /	AS
	THE TESTING MEDIUM ^D				· _ · · · · · · _ / · · /	

Amt of Alginate Analyzed (g/L)	mg BOD ₅ /g of Alginate	Average	Range of Average Values
2.5	20, 18, 16	18	12-18
5.0	13, 13, 9	12	

Amt. of Alginate Analyzed (g/L)	mg BOD ₅ /g of Alginate	<u>Average</u>	Range of <u>Average Values</u>
2.5	14, 12, 12	13	8-13
5.0	9, 9, 7	8	

TABLE X.	RESULTS OF THE BOD	ANALYSIS OF	ALGINATE	USING BOD	DILUTION
	WATER AS THE TESTIN	G MEDIUM			

Amount of Scrap Analyzed (g)	mg COD/g of Scrap	<u>Average</u>	Range in Replicate Values
0.05	416, 410, 413	413	
0.10	397, 355, 349	367	349-416

TABLE XI. RESULTS OF THE COD ANALYSIS OF GROUND CRAB SCRAP

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Amt. of Alginate Analyzed (g/L)	mg COD/g of Alginate	Average	Range in Replicate Values
0.5	424, 410, 418	422	
	429, 430		403-430
٥.١	414, 408, 403	410	
	407, 416		

TABLE XII. RESULTS OF THE COD ANALYSIS OF ALGINATE

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These solutions were sampled on Days 0, 1, 2, 4, 6, and 8, in an attempt to determine the adsorptive capacity and the rate of adsorption of Cd by the shell material.

Figures 41, 42, 43, and 44, show the percent of Cd which was removed from the solutions by the crab shell on each of the sampling dates. Note that the larger the quantity of shell material present, the greater the percent removal on Day 1. With 0.5 g of shell present, only 27 percent of the Cd was removed by Day I, whereas when 32 g of shell was present, 90 percent of the Cd was removed by Day 1. It should also be noted that all of the systems reached equilibrium within eight days, except those which contained only 0.1 g and 0.5 g of shell.

Figure 45 shows the percent of Cd removed by the varying quantities of shell after eight days.



Figure 41. Uptake of Cd by crab shells over an eight day period.



Figure 42. Uptake of Cd by 8 g of crab shell over an eight day period.



Figure 43. Uptake of Cd by 16 g of crab shell over an eight day period.



Figure 44. Uptake of Cd by 32 g of crab shell over an eight day period.



Figure 45. Levels of Cd adsorbed by various amounts of crab shell after eight days.

VI. DISCUSSION

This chapter will follow the format used in the "Results" chapter. The field studies will be discussed, followed by the tank studies, then an analysis of the oxygen demand data and, finally, the Cd uptake study. All of these areas will then be discussed jointly in an effort to relate the information to the problem of crab scrap disposal.

Field Studies

Field Study I

Because equipment was lost during this study, no specific data concerning scrap degradation were obtained. However, valuable knowledge concerning site location, containment device design and sampling techniques was gained.

It was determined that any future sites should be located in areas which experienced milder current action and less recreational traffic. The design of the containment device would need to be altered so that the scrap would be securely contained in the devices. These devices would also need to be anchored with extra weights to assure that they would remain at the sites. To assure that the sites would not be inadvertently changed during sampling, an anchorage system was designed which allowed one weight to always remain on the bottom. This knowledge was then applied

in the subsequent studies.

Field Study II

Both the coated and the uncoated scrap balls at each of the three sites degraded at similar rates, indicating that the alginate coating did not noticeably alter the degradation rate of the scrap ball.

The scrap was examined on Days 1 and 10 of this study and because no tissue was found on Day 10, it was determined that to properly define the rate of tissue loss, the scrap would have to have been examined more frequently. This problem was subsequently addressed in Field Study III.

The concentrations of Cd and Zn in the shell decreased with time. This would indicate that as the shells degraded, these metals were being released to the water and sediment. However, the impact on the water and sediment was not detected due to the relatively small contributions of Cd and Zn from the shell.

Field Study III

An approximation of the rate of tissue loss from both coated scrap balls and loose scrap was made in this study. For the coated scrap balls, six days were required for over 95 percent of the tissue contained in five, 300 g scrap balls to be lost from the containment devices. Approximately

85 percent of the loose scrap tissue, which had been attached to the shell, was lost after six days. There are several physical, biological, and chemical factors which might have affected the rate of tissue loss.

One physical factor is the tidal current. As the water flowed through the containment devices, it produced frictional forces on the exterior surfaces of the scrap. This contributed to the degradation of the coating and the scrap ball. The moving water also provided a mode of transport for the scrap particles. The scrap was also affected by a physical force which was created during each inspection. Each time a device was raised or lowered, water would be forced into or out of the container. This water created a flushing action and caused the loss of a significant portion of tissue upon each inspection.

The biological processes acting on the tissue were attributed to the organisms which were small enough to enter the containment devices, i.e., microinvertebrates, bacteria, and fungi. These organisms may have been feeding on the scrap. A new supply of organisms was constantly provided by the tidal current. Some macroinvertebrates were also found inside the containment devices. These were mainly isopods, amphipods, and marine worms.

The corrosive chemical nature of the saline water may have contributed to the degradation of the alginate coating

and the pitting seen in the whole crab shells.

Tank Studies

Tank Study I

In this portion of the work, the impact of three methods of crab scrap preparation on water quality were studied.

Raw, uncompacted scrap was used in Tank A. It was thought that this form would create the greatest impact on water quality and would be the least acceptable for offshore disposal.

The scrap in Tank B had been compacted. During the compaction process, much of the liquid in the scrap was removed. This liquid undoubtedly contained a considerable amount of organic matter and was one of the main components of the scrap responsible for the deterioration of the water quality in Tank A.

The scrap in Tank C had been both compacted and coated with an alginate gel. In this process, liquids were removed from the scrap and then the remainder of the scrap was encased in alginate. It was expected that this coating would encase the tissue and decrease the degradation rate of the scrap. Scrap in this form was expected to produce less of an impact on water quality and be the most acceptable form for offshore disposal. The observed impact of the scrap on the water quality in each of the three tanks corresponded well with the expected impacts. Tank A exhibited concentrations of NH_3 , TOC, and BOD and turbidity that were at least four times greater than those in Tank C and twice as great as those in Tank B.

The sensory observations also provided important information concerning these three scrap forms. The odor and visual appearance of the water indicated that the water in Tank A was most severely impacted by the scrap, followed by the waters of Tank B, and then Tank C.

Floating scrap is a major concern. Tank A contained the most floating scrap and it remained afloat the longest. However, the coated scrap was buoyant when first placed in Tank C, and it follows that if this coated scrap were to be placed in a denser liquid, such as seawater, it might not sink. Also, a section of this scrap did begin to float on Day 34, due to organic decomposition and gas production within the alginate coating.

<u>Tank Study II</u>

In this portion of the work, the impact of alginate coated scrap on four different simulated marine environments was studied.

Tank D, which was aerated and did not contain sediment, and Tank E, which was aerated and contained sediment, behaved almost identically, which indicates that the presence or absence of sediment did not markedly affect the impact of crab scrap on a well aerated system. Tank F, which contained sediment and was not aerated, and Tank G, which did not contain sediment and was not aerated, behaved in similar manners. However, differences that were attributed to the presence of sediment were reflected in the data for turbidity, dissolved oxygen, and nitrogen-containing compounds.

There were marked differences concerning the nitrogencontaining compounds in the aerated tanks, Tanks D and E, and in the non-aerated tanks, Tanks F and G. In the aerated tanks, the conditions were favorable for the growth of nitrifying bacteria. These bacteria converted the ammonia to $NO_2^- + NO_3^-$. The nitrifying bacteria could not function in the non-aerated tanks due to the anaerobic conditions. Therefore, the ammonia levels remained high and only very small amounts of $NO_2^- + NO_3^-$ were detected.

The cycling of these nitrogen-containing compounds is extremely important because of the high organic nitrogen content of the crab scrap. If too large a quantity of scrap is deposited at one site, the ammonia levels will increase rapidly from the conversion of organic nitrogen to ammonia under aerobic or anaerobic conditions. Ammonia is

toxic to fish and the increased concentrations may result in fish kills. Also, if the disposal site is aerobic, the ammonia will be converted to $NO_2^- + NO_3^-$, consuming the available oxygen. The reduced oxygen concentration may also initiate a fish kill and severely affect other aquatic organisms.

The NH₃ and organic nitrogen concentrations were consistently higher in Tank F and in Tank G. This could be due to the presence of a larger anaerobic microbial population or due to NH₃ and organic nitrogen release from the sediment.

The $NO_2^- + NO_3^-$ concentration was lower in Tank F than in Tank G. This could be explained by the more rapid depletion of oxygen from Tank F, since oxygen is required for the conversion of NH_3 to $NO_2^- + NO_3^-$. The $NO_2^- + NO_3^-$ concentration noted in these tanks on Day 36 indicates that the carbonaceous BOD had decreased to the point that oxygen was then available to satisfy part of the nitrogenous BOD.

The turbidity in Tank F was greater than in Tank G, except on Days 2 and 3. This could be explained by the fact that, with sediment, there would be a larger and more stable anaerobic microbial population in Tank F than in Tank G. This population would tend to cause an increase in the turbidity due to the increased numbers of organisms in the water column.

The graphs of D.O. versus time show that the sediment exhibited a strong oxygen demand. Tank F was anaerobic

after one day, whereas Tank G remained aerobic until Day 3.

The sensory observations supported and expanded the analytical data. It was noted that in all the tanks the alginate coating had sloughed off of the scrap balls within four hours. This indicated that the alginate coating lost its integrity rapidly in the saline water.

All of the tissue seemed to have disappeared from Tank D and Tank E by Day 11. This observation supports the analytical data which indicated a marked improvement in the water quality of these tanks after Day 11.

Oxygen Demand Study

BOD Analyses

The BOD_5 of the scrap varied from 141 to 278 mg per g of scrap. The actual value obtained for any given analysis was dependent upon the amount of scrap analyzed. The less scrap analyzed, the higher and the more variable the BOD_5 values. The higher values could have been due to the fact that the larger samples seemed to have a higher shell-to-tissue ratio and therefore would exert less BOD. The greater variability could be attributed to the inaccuracy of both the BOD_5 testing procedure, the weighing of such small amounts of scrap, or some inhibitory agent present in the scrap, such as heavy metals.

The BOD_5 of the alginate varied from 7 to 20 mg of BOD_5 per g of alginate. The variability noted in this analysis can be contributed to the variability which is inherent to the BOD_5 test. In comparing the results of the analyses using seawater with the analyses using BOD dilution water, it was found that there were no major differences between the two methods.

COD Analyses

The COD of the scrap varied from 349 to 416 mg of COD per g of scrap. This variation was also thought to be attributable to fluctuations in the shell-to-tissue ratio which was seen in samples that differed in size.

The COD of the alginate varied from 403 to 430 mg of COD per g of scrap. This is quite similar to the COD of the scrap.

The BOD₅ and COD of the scrap were reported in ranges to take into account the variability in the shell-to-tissue of crab scrap. This shell-to-tissue ratio of the scrap is dependent on the season of the year, the area which it is from, and the picking process used. If the scrap is from an area having water of a higher salinity, the crab scrap produced in the spring will possess a much lower shell-totissue ratio. This is due to the fact that the female requires higher salinity waters to properly develop her egg

masses and these are developed in the spring (2). These egg masses are discarded with the scrap which, in turn, lowers the shell-to-tissue ratio. The crab picking process that is used can also affect the shell-to-tissue ratio of the scrap. Crab picking can be either hand picking of the entire crab or mechanical picking of just the crab claw. Hand picking is usually the most efficient and produces the largest shell-to-tissue ratio. Thus, due to the high variability of crab scrap, no one COD or BOD₅ value can be assigned to it.

Cadmium Uptake Study

The purpose of this study was to determine if the shell material in the crab scrap would adsorb Cd. The data indicated that crab shell is an excellent adsorbent for Cd.

The maximum amount of Cd adsorbed per g of shell was 0.564 mg. This was observed in a batch reactor which contained only 0.5 g of shell and 2 mg/L of Cd. The 0.564 mg of Cd was adsorbed by Day 8. However, this value probably underestimates the adsorptive capacity of the shell because equilibrium had not been reached by the time the sample was sacrificed.

In the batch reactors which contained more than 2.0 g of shell, each system reached equilibrium by Day 6. In all of these reactors, except the one containing 8.0 g of shell,

equilibrium was reached after 90 percent of the available Cd had been removed from the solution. The maximum percentage removal was 98 percent, and this efficiency was observed in both the batch reactor containing 16.0 g of shell and the one containing 32.0 g of shell.

In the three batch reactors which attained equilibrium (4.0 g, 16.0 g, and 32.0 g of shell), the amount of Cd remaining in the solution at equilibrium ranged from 0.011 mg and 0.019 mg, which was equivalent to 0.07 mg/L to 0.13 mg/L.

Recommended Disposal Procedure

After investigating the individual areas of concern, the entire offshore disposal procedure must be considered. In order to accomplish this, a proposed disposal procedure is outlined below and the reasoning behind each step is given.

After the crabs are picked, it is recommended that the scrap be ground into pieces smaller than 0.6 cm^2 . This grinding process reduces the volume of the scrap by approximately a factor of five and therefore makes the scrap easier to transport to the disposal site.

Following the grinding process, the scrap should be allowed to fall from the grinder into sealable containers for transport. The scrap must be sealed in some way during transport to reduce the odor associated with the scrap. It is suggested that an alginate gel be used for sealing the surface of the scrap in the reusable container before the lid is put in place. This reusable container could then be hoisted onto a boat or barge and taken to the disposal site where the contents would be dumped.

After dumping, it is expected that the ground crab scrap would sink. As the ground scrap sinks through the water, some of the less dense particles of tissue would be transported from the disposal site by the currents, while the more dense particles of shell would sink to the bottom. This dispersion of tissue would decrease the amount of BOD and COD exerted at the disposal site. The amount of tissue dispersed and, thus, the decrease in BOD and COD realized would be directly proportional to the velocity of the current at the disposal site.

Care must be taken throughout this disposal procedure to assure that the crab scrap does not become contaminated with Cd. The shell in the scrap readily adsorbs Cd and could release it as the shell degraded in the aquatic environment. If contamination, uptake, and release of Cd occurred, the ecosystem at the disposal site could be severely impacted.

Proper management of the offshore disposal system is the key factor to its environmental success. The scrap preparation process must be carefully controlled. The dis-

posal sites must be properly chosen considering the current velocity, depth, mixing action, and D.O. concentrations. Proper rates of scrap application must be assigned to each disposal site to prevent deterioration of the ecosystem. Careful monitoring of the disposal process and water quality at the disposal sites is required. If these proper management procedures are instituted, it would appear that crab scraps may be disposed of at sea.

VI. SUMMARY AND CONCLUSIONS

Among the problems associated with the offshore disposal of crab scrap are the odor, volume, and handleability of the waste, the presence of floating matter at the disposal site, and the impact of the waste on water quality. Crab scraps exert a relatively high oxygen demand, release ammonia and oxidized nitrogen during decomposition, and have a high affinity for heavy metals.

After identifying these problems, a means of handling the crab scrap had to be developed which would minimize these problems. Compaction of the crab scrap was thought to be a possible means of reducing the volume; however, following this work it is felt that the costs of compacting the wastes under high pressures outweigh the benefits derived. These costs include the high capital cost of the equipment, the high energy costs for operation of the equipment, and the cost of sewering or pretreating the high BOD liquid waste.

Another method for reducing the crab scrap volume was therefore considered and consisted of grinding the scrap. Grinding reduced the volume by a factor of five and eliminated the problem of floating scrap. The ground crab scrap could be deposited directly in a reusable container and sealed with an alginate gel to reduce odor and then trans-

ported to the disposal site. The alginate was found to have a low BOD₅ and would therefore, probably not increase the oxygen demand at the disposal site.

The ground crab scrap would produce a less severe impact on the water quality than would whole scrap. This is because, as the ground scrap sinks through the water, some of the less dense particles of tissue would be transported from the disposal site by the currents. The dispersion of tissue would decrease the amount of ammonia and oxidized nitrogen produced and the amount of BOD exerted at the disposal site, thus reducing the impact of the scrap on the water quality.

In conclusion, the following statements can be made:

- Several potential water quality problems are associated with the offshore disposal of crab scrap. They are the shell materials affinity for heavy metals, the high oxygen demand exerted by the scrap, and the production of potentially toxic amounts of ammonia and oxidized nitrogen.
- The grinding of the crab scrap reduced the volume and eliminated the problem of floating scrap.
- 3. The alginate gel used to seal the scrap and prevent odor problems did not add appreciably to the short term oxygen demand of the crab scrap.

4. The alginate gel coating did not appreciably delay
the degradation of the ground scrap because the alginate coating lost its integrity and was readily dispersed in the saline environment.

It is therefore believed that crab scraps may be disposed of in marine environments provided that appropriate disposal sites are selected and properly managed; i.e., careful monitoring of disposal techniques and water quality at the disposal sites.

VIII. REFERENCES

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APPENDIX A PROCEDURES

HACH MANOMETRIC BOD APPARATUS

Principle of Operation

A measured amount of crab scrap is placed in one of the bottles, to which dilution water has been added. The bottle is then placed on the stirring apparatus and connected to a closed end mercury manometer. Above the crab scrap solution is a quantity of air which contains 21 percent oxygen (13). Over a period of time, bacteria in the solution utilize oxygen to oxidize organic matter present in the crab scrap, and thus dissolved oxygen is consumed from the sample. The air in the closed sample bottle replenishes the utilized oxygen which results in a drop in air pressure in the sample bottle (13). The pressure drop is registered on the mercury manometer which can be read directly as mg/L BOD. The sample is continually agitated during the test period by a magnetic stirring bar. Carbon dioxide is produced by the oxidation of organic matter and must be removed from the system in order that it does not develop a positive gas pressure that would result in an error. This is accomplished by placing a cup with potassium hydroxide into the sample bottle, being sure that it does not come in direct contact with the sample (13).

APPENDIX B

EXPERIMENTAL DATA

TABLE A-1. WATER QUALITY DATA FOR THE FIRST SIX DAYS OF TANK STUDY I

		Ω	ay l Tank		Da	y 2 ank		Da	y 3 ank			ay 4 Tank		Da	ly 5 ank		Day Tan	يد م	
	All Tanks	A	æ	ى	A	æ	J	A	B	ں ا	A	8	u	A	m	J	A B	C L	
Organic N (mg/L as N)	3.0	I	1		21	1.7	1.0	14	2.2	1.4	19	4.8	1.0	24]	.7 1	0.	1	I	
NH ₃ (mg/L as N)	1.0	5.5	З.б	5< 1.0	8.9	4.4	2.3	Ξ	4.4	2.1	22	13	5.3	33	19 6	.82	919	6.4	
D.O. (mg/L)	8.2	6.2	7.6	5 80	7.6	8.1	8.2	8.2	8.4	8.4	8.]	8.4 8	3.0 8	3.2 ε	3.18	.17	.88.	18.1	
Temperature (^O C)	23	23	2	3 23	22	22	22	22	22	22	23	23	23	21	21	212	1 21	21	
Turbidity (NTU)	0.4	17	5,(01.8	22	9,2	3.8	18.5	7.5	3.6	22	15 !	5.6	30	12 6	.33	3 13	6.5	
hd	7.0	7.0	7.(0.7.0	6.9	5.5	6.5	7.5	7.7	7.6	7.2	7.5	7.6	7.5	7.6	7.6	7.7	7.97	۲.
TOC (mg/L)	1.3	42	6 1	б	20	14	Q	19	13	9	21	15	ß	22	28	5	25	17	ß
BOD ₅ (mg/L)	12	84	36	<12	53	23	<12	46	27	<12	130	34	<12	4]	28 <	ן 2 ר	75	35<11	2
						·													

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TABLE A-2. WATER QUALITY DATA FOR THE FIRST SIX DAYS OF TANK STUDY II

		TANK D			TANK E			TANK J	. . !		TANK	G
DAYS	Repo	vrted in mg/	'L as N	Repo	rted in mg/	L as N	Repor	ted in mg/	/L as N	Repor	ted in mg	/L as N
	NH ₃	$NO_2^{-} + NO_3^{-}$	Org.N	ени ³	$NO_2 + NO_3$	Org.N	NH ₃	$NO_{2}^{-} + NO_{3}^{-}$	Org.N	. HN	201 + 201	Org.N
0	2	~	4 >	~		4	, ∴	י בי נ	V	ک د		
-	22	2	2	13.5		< 4	~ ~	- ~	1 4	7.6	7 5	5 5
2	25	~	4.5	23	~	18	26	. <u>^</u>		25	7 7] 2 E
с С	33	~	4.8	31	ŗ	5.7	15	[>	2 7	<u>,</u>	7 7	0
£	45	<u>د</u> ا	<4	4]	ب	4	19	· [~	- œ	ງ ແ ເ	7 7	0 5
٢	62	<]	ł	57	ę	ı	37	2	4.6		- ~	ţ
6	59	6	<4	61	n	4×	40	- 2	2	24	J -	· •
Ξ	37	9	3.3	55	~	7.5	52	' 🟹	8 [[24	* ⊽	, c
13	13	20	2.1	40	12	×4	52	2	6.3	5 12		л г с 7
16	4	29	4 >	13.5	23.5	· † >	5]	Ļ		3 6		- U •
19	$\overline{}$	17	<4	~	17	<4	61	· ·	2 4 - v		- \	0 73
22	Ļ	27	<4	~	25	×4	63		1.8		7 7	4 4
27	~	22	4×	Ċ	14	<4	64	~	3.2	56		ο ~ • α
36	7	33	4>	Ļ	13	<4	62	9	1.7	63	, 6 ,	2.9

IANK G	<pre>emperature D.0. (C) (mg/L)</pre>		26 5.0	26 5.0 26 3.6	26 5.0 26 3.6 24.5 3.6	26 5.0 26 3.6 24.5 3.6 26 1.0	26 5.0 26 3.6 24.5 3.6 26 1.0 26 1.0 25 1.0	26 5.0 26 5.0 24.5 3.6 26 1.0 26 1.0 25 1.0	26 5.0 26 5.0 24.5 3.6 26 1.0 26 1.0 25 1.0 26 1.0 27 1.0	26 5.0 26 5.0 24.5 3.6 26 1.0 26 1.0 25 1.0 26 1.0 26 1.0 26 1.0	26 5.0 26 5.0 26 3.6 24.5 3.6 26 1.0 25 1.0 26 1.0 26 1.0 26 1.0	26 5.0 26 5.0 26 3.6 26 1.0 26 1.0 26 1.0 26 1.0 26 1.0 26 1.0 26 1.0	26 5.0 26 5.0 26 3.6 26 1.0 26 1.0 26 1.0 26 1.0 26 1.0 26 1.0 26 1.0	26 5.0 26 5.0 26 3.6 26 1.0 26 1.0 26 1.0 26 1.0 26 1.0 26 1.0 26 1.0 27 1.0 27 1.0 27 1.0 27 1.0	26 5.0 26 5.0 26 3.6 26 1.0 25 1.0 26 1.0 26 1.0 26 1.0 26 1.0 26 1.0 27 1.0 27 1.0 27 1.0 27 1.0
	TOC Te mg/L)	10	01	79	13	12	39	53	27	00	77	6L	61 61	25 25	25 17 19
	D.0. (mg/L)(2.6	1.0	1.0	1.0	1.0	1.0	1.0	1.0	U L	,	0.1	0.1 0.1	0.1 0.1	1.0 1.0 1.0
<u>TANK</u> F	Tempe Sature (C)	26	26	25	26	25	26.5	27	26	27		27	27 26	27 26 27	27 26 27
	. TOC .	10	17	15	11	49	24	24	27	13		27	27 25	27 25 21	27 25 21 17
	D.0. (mg/L.)	5,8	4.4	4.8	4.6	5.6	5.4	5.6	5.5	5.1		5.5	5.5 5.8	5.5 5.8 5.7	5.5 5.8 5.7 5.6
LANN E	Tempeçature (^C C)	26	26	25	26	25	27	27	27	27		27	27 26	27 26 27	27 26 27 27
	T0C (mg/L)	10	20	32	22	26	26	21	20	14		14	14 13	14 13 13	14 13 13 21
	D.O. (mg/L)	6.0	4.5	4.9	5.3	5.3	5.1	5.6	5.5	5.4		5.5	5.5 5.8	5.5 5.8 5.7	5.5 5.8 5.7 5.8
IANN D	Temperature (^C C)	26	26	25	26	25	26	27	27	27		27	27 26	27 26 27	27 26 27 27
	T0C (mg/L)	01	30	26	28	28	28	27	20	17]6	16 16	16. 16	16 16 15
	Days	0	-	~	e	ഹ	7	σ	Ξ	13		J16	16 19	16 19 22	16 19 22 27

TABLE A-2, CONTINUED

TABLE A-2, CONTINUED

		TANK D		TANK E		TANK F			TANK G	
DAYS	Ηd	Turbidity (NTU)	Hq	Turbidity (NTU)	Hd	Turbidit, Surface	r (NTU) Bottom	Hd	Turbidit Surface	y (NTU) Bottom
0	7.8	1.2	7.9	17	7.5	5,0	5,0	7.8	0.9	6.0
	7.5	21	7.4	15	7.2	4.4	4.4	7.5	1.7	4.7
2	7.9	15	7.8	וו	7.4	3.1	13	7.9	ו.ו	52
e S	7.9	5,5	7.9	10	7.1	3.9	17	7.4	1. 1	43
S	8.1	8.0	8.1	8.4	6.7	3.7	10	6.9	1.5	7.4
7	8.]	8.5	8.2	8.5	6.7	3.7	17	6.9	2.0	18
6	8.0	13	8.2	8.0	6.8	8.4	28	6.9	2,6	12
П	1.7	1.5	8.3	9.5	7.0	25		7.0	5.0	17
13	7.8	1.7	8.2	2.2	7.0	13		7.0	9	0.0
16	8.0	1.4	8.2	1.7	۲.٦	40		۲.٦	9	.7
19	8.2	1.0	8.2	1.3	7.3	60		7.1	6	.5
22	8.3	0.7	8.3	0.8	7.3	1		7.1		ı
29	8.4	0.5	8.3	0.5	6.3	. 29		6.5		12
36	8.3	0.4	8.4	0.7	۲.٦	26		7.6		10

THE IMPACT OF CRAB WASTES ON MARINE ENVIRONMENTS

PART II

PROJECT REPORT

Part II. The Impact of Crab Wastes on Marine Environments

Project No. F19-82-00815

Submitted by:

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Date:

May, 1983

INTRODUCTORY REMARK

The following paper constitutes Part II of the final report for project F19-82-00815, "The Impact of Crab Wastes on Marine Environments." In this portion of the report the results of efforts to compact crab scraps for overboard disposal are described.

MATERIALS AND METHODS

Crab scraps from a commercial crab processing plant in Hampton, Virginia were collected immediately after picking and transported on ice to Blacksburg, Virginia where they were frozen at -20°C until needed. Compressed blocks were prepared from the cold defrosted scraps by first grinding the scraps in a 1 HP commercial meat grinder with a 1/4 inch perforated face plate. Fresh crab scrap blocks (FR) were prepared from the scraps immediately after grinding. Stored crab scrap blocks (ST) were prepared from the ground product after 5 days of storage at 4.4°C. Block Construction

The ground crab scraps were thoroughly mixed with various binders, placed in a specially constructed compression cell, and compressed in a Carver hand press to 15,000 psi with a 50.8 mm diameter ram for a 5 minute holding period. The cell was cylindrical and built of polished steel, with walls 22 mm thick, an inside diameter of 51 mm, and a height of 343 mm. Compressed blocks were placed in a convection oven and dried at 90°C for 12 hours. After cooling the blocks were weighed, measured, and then immersed in Nalgene tanks (see Tank Studies Section).

The following binders were mixed with the scraps:

- a. <u>Treatment A</u> <u>Speed Plug powder</u>, manufactured by Taams Industries, Illinois and California, generally used as a quick setting hydraulic cement to stop leaks in concrete and masonry;
- <u>Treatment B</u> <u>MC-46 powder</u>, manufactured by Rohm and Haas,
 Pennsylvania, a modified acrylic cement used to improve adhesion and increase strength of cement mortar;
- c. <u>Treatment C</u> <u>Rhoplex E-330 liquid</u>, manufactured by Rohm and Haas, a water dispersion of acrylic polymer used to improve textural adhesive and impact strengths of Portland cements;
- <u>Treatment D</u> <u>DLR-MR</u>, 40% solution manufactured by Rohm and Haas, a blend of off-grade water emulsified acrylic resins used as a binder to prevent soil erosion;
- e. <u>Treatment E</u> <u>Kelco Gel HV</u>, 2% solution, manufactured by Kelco, New Jersey, a refined high viscosity sodium alginate used as a stabilizing, binding, and gelling agent by the food industry.

The powders were mixed at a ratio of 20 g binder to 80 g of ground scrap, while the liquids were mixed at a ratio of 20 g binder to 100 g of scrap.

Shelf Life

Dry blocks were placed on a shelf at room temperature for two months to monitor offensive odor production. Six blocks of each treatment were placed in a room 5 by 10 feet.

Tank Studies

Five gallon Nalgene tanks were used to study the behavior of the crab scrap blocks in water. The tanks were filled with tap water and then the blocks were placed inside. The blocks floated initially, but sank within 24 hours and were spaced equally apart in the bottom of the containers. The tanks were kept covered throughout the experiment.

Duplicate samples of bottom and surface water (150 ml each) were withdrawn with long pipettes from the tanks and placed into sealed containers for subsequent chemical determinations. Tap water was added to each tank to replace water losses due to sampling and evaporation. At the end of the submersion period, the blocks were removed from the tanks and allowed to drain for 12 hours. The drain water and blocks were weighed and the block heights and diameters were recorded. The force required to shear each block was determined using a 5,000 lb ring and a standard shear cell with a Kramer-Alloe shear press.

An Orion 901 Analyzer with specific ion electrodes was used to determine the concentrations of nitrate, ammonia, and sulfide in the water samples. The concentrations of the three compounds versus the number of days blocks were stored in the tanks were plotted using the SAS computer package. A cubic spline method with continuous derivations using a third degree polynomial for each set of two adjacent points was used to graph the curves.

RESULTS

Curves for nitrate production are presented in Figure 1 (A-E). Tanks containing fresh and stored crab scrap blocks were monitored for



Figure 1AF. Nitrate levels in treatment A experiment with fresh blocks; top sample = ____, bottom sample = ____.

NO₃-N conc., mg/L



Figure IBF. Nitrate levels in treatment B experiment with fresh blocks; top sample = ---, bottom sample = ____.



Figure ICF. Nitrate levels in treatment C experiment with fresh blocks; top sample = ---, bottom sample = ____



Figure 1DF. Nitrate levels in treatment D experiment with fresh blocks; top sample = ---, bottom sample = ____



Figure 1EF. Nitrate levels in treatment E experiment with fresh blocks; top sample = ---, bottom sample = ____.







Figure IBS. Nitrate levels in treatment B experiment with stored blocks; top sample = ---, bottom sample = ____.



Figure I(S. Nitrate levels in treatment B experiment with stored blocks; top sample = ---, bottom sample = ____.



Figure 1DS. Nitrate levels in treatment B experiment with stored blocks; top sample = ---, bottom sample = ____.



Figure 1ES. Nitrate levels in treatment E experiment with stored blocks; top sample = ---, bottom sample = ____.

nitrate production on six occasions. Tanks with fresh blocks were monitored after 3, 6, 8, 13, 19, 22, and 29 days, and the tanks with stored blocks were monitored after 5, 10, 15, 19, 24, 28, and 35 days.

Nitrate levels in the tanks containing fresh blocks increased slightly around the 5th day and decreased after approximately 10 days followed by a sharp increase. In the tanks with stored blocks a fairly sharp peak developed on the 12th day and a decrease around the 20th day was followed by a rise in nitrate level.

In all cases higher concentrations of nitrate were found in the bottom samples than in the surface samples. Depending on the treatment the nitrate levels ranged from 120 to 630 mg/L in the surface samples and from 135 to 960 mg/L in the bottom samples. The lowest amounts of nitrate in the bottom samples were produced in Treatment A, reaching a maximum of 130 and 134 mg/L for the fresh and stored scrap blocks, respectively. The highest amounts of nitrate were generally produced in the bottom samples. Treatment D reached a maximum of 930 and 960 mg/L in the fresh and stored blocks, respectively. Treatment C produced 730 and 810 mg/L nitrate for the fresh and stored blocks, respectively. Treatment E produced 670 and 620 mg/L for the fresh and stored blocks, respectively; whereas, Treatment B produced 650 and 520 mg/L nitrate for the fresh and stored blocks, respectively. The increases in nitrate production coincided with increasing microbiological growth.

Curves for ammonia production are presented in Figure 2 (A-E). Tanks containing fresh and stored crab scrap blocks were monitored for ammonia production on 5 and 9 dates, respectively. The tanks with fresh



Figure 2AF. Ammonia levels in treatment A experiment with fresh blocks; top sample = ---, bottom sample = ____.



Figure 2BF. Ammonia levels in treatment B experiment with fresh blocks; top sample = ---, bottom sample = ____.

NH₃-N conc., mg/l.



Figure 2CF. Ammonia levels in treatment C experiment with fresh blocks; top sample = ---, bottom sample = ____.



Figure 2DF. Ammonia levels in treatment D experiment with fresh blocks: top sample = ---, bottom sample = ___.



Figure 2EF. Ammonia levels in treatment E experiment with fresh blocks; top sample = ---, bottom sample = ____.



Figure 2AS. Ammonia levels in treatment A experiment with stored blocks; top sample = ---, bottom sample = ___.







Figure 2CS. Ammonia levels in treatment C experiment with stored blocks; top sample = ---, bottom sample = ___.



Figures 2DS. Ammonia levels in treatment D experiment with stored blocks; top sample = ---, bottom sample = ____.



Figure 2ES. Ammonia levels in treatment E experiment with stored blocks; top sample = ---, bottom sample = ____.
crab scrap blocks were monitored after 3, 5, 9, 13 and 22 days; and, the tanks with stored crab scrap blocks were monitored after 3, 6, 9, 11, 17, 20, 26, 28, and 35 days.

As can be seen from the ammonia production curves (Figure 2, A-E), the tanks with fresh blocks exhibited a sharp increase in ammonia around the 8th day with a dip around the 16th day. This decrease was followed by another steep increase. In the tanks with stored blocks a sharp peak in ammonia occurred around the 9th day, but levels fell rapidly through to the 14th day and then started to rise again.

In all cases, higher amounts of ammonia were found in the bottom samples than in the surface samples. Ammonia levels ranged from 220 mg/L to 1,350 mg/L in the surface samples and 300 to 4,350 mg/L in the bottom samples. The lowest amounts of ammonia in the bottom samples were produced in Treatment A, reaching a maximum of 300 and 375 mg/L for the fresh and stored scrap blocks, respectively. The highest amounts of ammonia were produced in Treatment E, attaining concentrations of 4,350 mg/L for the fresh scrap blocks and 3,000 mg/L for the stored blocks. The levels of ammonia in Treatment C reached 2,550 for the fresh blocks and 3,250 mg/L for the stored blocks. Treatment D ammonia levels reached 2,550 mg/L and 3,450 mg/L in the tanks containing fresh and stored blocks, respectively.

Curves for sulfide production are presented in Figure 3 (A-E). Only tanks with stored scrap blocks were monitored for sulfide production on 6 dates. These tanks were monitored after 7, 12, 21, 26, 31, and 38 days. As can be seen from the curves for sulfide production,







Figure 3BS. Sulfide levels in treatment B experiment with stored blocks; top sample = ____ bottom sample = ____.



Figure 3CS. Sulfide levels in treatment C experiment with stored blocks; top sample = ---, bottom sample = ____.



Figure 3DS. Sulfide levels in treatment D experiment with stored blocks; top sample = ---, bottom sample = ____.





low peaks generally developed after 17 days, except for one treatment that had its first sulfide peak on the 12th day and then there was a dip on the 25th day for all the treatments. A steep peak developed on the 32nd day which then decreased again on the 38th day.

The partitioning of sulfides in teh upper and lower regions of the tanks varied, but appeared to be related to the type of block treatment. There was generally a low level of 100 to 200 mg/L between the 15th and the 20th day of submersion (except for Treatment A where the peak occurred on the 13th day), and then a sharp increase on the 32nd day, followed by a pronounced decrease in concentration on the 38th day. The lowest levels of sulfide were produced in Treatment A and E, reaching 400 and 375 mg/L, respectively. The highest amounts were produced in treatments B and C, 700 and 650 mg/L, respectively. Treatment D yielded a maximum of 500 mg/L of sulfide.

The tanks were also monitored for oxygen content and, as expected, the tanks were anaerobic when nitrates, ammonia, and sulfides were present in the greater concentrations.

Table 1 contains the crab scrap block weights and dimensions before and after immersion in the tanks. Before immersion, all blocks did not weigh the same and the first column in Table 1 illustrates the differences which were noted. Treatment A yielded the heaviest blocks, but there appeared to be no real differences among the other treatments. Additionally, Treatment A blocks were shorter in height than the blocks for the other treatments indicating a greater compaction for Treatment A. Note that Treatment E blocks were tallest. The diameters of the

Table]. Range of Crab Scrap Block Weight, Dimension, and Water Uptake in Tanks.

Treatment*	Initi [ial Weights Dimensions	and		Weights a One	nd Dimensi Month in T	ons After anks	
<pre>(6 blocks/ treatment)</pre>	Weight. 9	Height, mm	Diam., nm	Weight, g	Height, mm	Diam.,	gain gain	<pre>% Drainage overnight</pre>
a fr a st	51-52	28-30 "	50-51	76-79 82-85	33-34 32-36	52 52-53	33-35 37-39	00
B FR B ST	41-47 49-50	31-32 "	50-51	73-79 76-79	42 39-42	51-52	38-40 36-37	0.3-4 0-0.7
c FR c ST	44-48 41-47	35-36 "	- 2	59-67 69-71	33-45 37-39	51-56 48-52	24-28 37-41	0.6-3 2-5
D FR D ST	4]-46 4]-47	33-34 "	53	62-63 64-71	36~38 37-39	5254 48-50	28-33 34-37	1-7 3-5
E FR E ST	42-43 38-39	40-41	50 "	+ :	+ - =	÷ =	+ =	÷ =
*FR = fresh b †Blocks disin	lock; ST = st tegrated in t	tored block. tanks.						

blocks were similar, except for Treatment D blocks which appeared to expand somewhat after compaction.

Following immersion, all blocks experienced about a 33 percent weight gain through water absorption. Except for Treatment B, the stored blocks absorbed more water than the fresh blocks. Blocks from Treatment C and D contained more water than Treatments A and B blocks. Treatment C stored crab scrap blocks gained 37-41 percent of their weight in water as compared to 24-28 percent for the fresh scrap blocks. In Treatment D, the percentage for the stored blocks was 34-37 percent, as compared to 28-33 percent for the fresh blocks.

The blocks in Treatments A through D swelled, while those of Treatment E disintegrated during the last week of submersion. Swelling was generally in height, rather than in diameter, reaching an average increase of 25 percent in Treatment B followed by 13 percent in Treatment A. The blocks in Treatments C and D increased an average 9 percent in height.

Drip loss differed among the treatments. There was no drip from Treatment A blocks which retained almost all absorbed water. Treatment D losses from both fresh and stored scrap blocks were greatest, averaging 3.5 and 4 percent, respectively. This was followed by Treatment C with averages of 2 to 3 percent and Treatment B with 2 and 0.7 percent losses, respectively. Generally drip losses did occur and the losses were greatest for the stored crab scrap blocks.

Table 2 provides the microbiological counts in the tanks at the end of the submersion period. Aerobic and anaerobic populations in the

	Bacteria Level, No./ml			
Treatment*	Aerobes	Anaerobes		
A Fresh (FR)	1.0 x 10 ⁶	3.0 x 10 ⁵		
A Stored (ST)	1.1 x 10 ⁸	1.9 x 10 ⁶		
B FR	1.1 x 10 ⁶	9.8 x 10 ⁵		
B ST	4.3 × 10 ⁸	3.4×10^7		
C FR	2.4 x 10 ⁶	4.9 x 10^5		
C ST	7.2 x 10 ⁷	1.3 x 10 ⁷		
D FR	3.6×10^{6}	7.0 x 10 ⁵		
D ST	1.6 x 10 ⁹	7.8 x 10 ⁷		
EFR	1.3 × 10 ⁶	2.6 x 10 ⁶		
E ST	1.2×10^8	4.0×10^{7}		
*FR = fresh blocks; SI	= stored blocks.	· · · · · · · · · · · · · · · · · · ·		

Table 2. Bacterial Levels in Tanks at End of Submersion Period.

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tanks with stored crab scraps were much higher than in the tanks with fresh blocks. Aerobic bacterial counts in the tanks with fresh blocks ranged from 1.0 x 10^6 to 3.6 x 10^6 per ml, and in the tanks with stored blocks the aerobic population ranged from 7.2 x 10^7 to 1.6 x 10^9 . Anaerobic counts in the fresh block tanks ranged from 3.0 x 10^5 to 2.6 x 10^6 per ml, as opposed to a range of 1.9 x 10^6 to 7.8 x 10^7 per ml in the stored block tanks. Treatment D tanks contained the highest aerobic counts for the fresh crab scrap blocks with a count of 3.6 x 10^6 per ml and also for the stored blocks with a count of 1.6 x 10^9 per ml. The greatest anaerobic bacteria levels for the fresh blocks were obtained in Treatment E, with a count of 2.6 x 10^6 per ml. The greatest anaerobic bacteria counts obtained with the stored blocks were noted in the Treatment D tanks $(7.8 \times 10^7 \text{ bacteria per ml})$. The lowest aerobic bacteria levels for fresh crab scrap blocks were noted in Treatment A $(1.0 \times 10^6 \text{ per ml})$, while Treatment C provided for the lowest aerobic bacteria levels with stored blocks (7.2 x 10^7 per ml). The lowest anaerobic bacteria counts for fresh and stored crab scrap blocks were detected in Treatment A $(3.0 \times 10^5 \text{ and } 1.9 \times 10^6 \text{ bacteria/ml},$ respectively).

Table 3 provides the shear forces required to shear the various blocks following their removal from the tanks. The toughest blocks, which did not shear even under a force of 5000 lbs, were those of Treatments A and B. Treatment E blocks were not tested because they disintegrated in the tanks. The fresh and stored scrap blocks of

Treatment	Shear (1bs)	AUC (circles)
A FR	> 5000	+
A ST	> 5000	· +
B FR	4554	1.38
B ST	> 5000	+ ·
C FR	1575	0.49
C ST	1691	0.41
DFR	1295	0.22
D ST	654	0.17
EFR	#	#
E ST	#	#

Table 3. Force Required to Shear Fresh and Stored Crab Scrap Blocks following Removal from Tanks.

*FR = fresh blocks; ST = stored blocks. #Off-scale with 5000 lb ring. #Block disintegrated in tanks.

Treatment C sheared at 1575 and 1691 lbs, respectively. The fresh and stored blocks of Treatment D sheared at 1295 and 654 lbs, respectively.

DISCUSSION

The data indicated that ammonia production by the fresh scrap blocks peaked on the 8th day, then dipped and rose again on the 16th day, while nitrate production increased slowly at first and then proceeded at an accelerated rate. With the stored crab scrap blocks, ammonia peaked around the 9th day with a secondary rise on the 20th day, while nitrate levels peaked on the 12th day with a second rise on the 20th day. Sulfides in the stored scraps peaked on the 17th and 35th days.

Increases in ammonia levels were probably due to the bacterial reduction of nitrate (Mortenson, 1962) and non-oxidative deamination (Moat, 1979). Sulfide production in the tanks probably resulted from bacterial breakdown of the sulfur-containing amino acid, cysteine, by deamination through cysteine desulfhydrase under anaerobic conditions (Moat, 1979).

The appearance of nitrates from the fresh and stored scrap blocks differed, being slow for fresh blocks and peaking after a week for stored blocks. This may indicate that different conditions for nitrate production were present. In the fresh scraps the build-up of electron acceptors for ammonia oxidation was slow, while the stored scraps had enough time to produce the necessary conditions for conversion of ammonia to nitrates. In comparing the data for microbiological counts, shear values, block dimensions, and water uptake, some points of interest were noted. First, the scrap blocks of Treatment E, which disintegrated in the tanks during the last week of submersion, had compacted poorly when compared to the other treatments. The disintegration was therefore partly due to the poorer binding properties of the agent used in Treatment E. The binder in this case appeared to give more "memory" to the block than the others had. The disintegration might also have been related to bacterial contamination, as indicated by the large numbers of anaerobes in the fresh and stored scraps of treatment E. Since all scraps were of the same origin, the Treatment E binder might have served as a good substrate for the flora which developed.

A second point of interest was the lower shear forces noted for treatment C and D blocks. This may have been a result of two factors. Treatment D blocks exhibited the lowest shear forces and the poorest water-holding capacities. These qualities coupled with the highest aerobic and anaerobic bacteria counts $(1.6 \times 10^9 \text{ and } 7.8 \times 10^7 \text{ per ml})$, respectively) appeared to be related to block disintegration. Blocks of Treatment C, which had the next lowest shear readings to Treatment D, also had the next highest water drainage losses (2 to 3.5 percent as opposed to 3.5 to 4 percent).

Treatment A blocks appeared to have the greatest ability to resist disintegration. These blocks compressed well, lost the least amount of water upon drying before submergence, and had good water holding capacity. Treatment A blocks maintained a very good resistance to

shear, and microbiological counts were relatively low in those tanks which contained the blocks.

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CONCLUSIONS

- Shelf stable, sinkable blocks of crab scrap can readily be prepared through grinding the scrap and adding various binding agents.
- Higher levels of bacteria, ammonia, nitrate, and sulfide appeared to be associated with stored scrap blocks than with fresh scrap blocks.
- 3. It appears that crab scrap blocks can be disposed of where there is adequate tidal flows allowing for the dispersion of produced ammonia, nitrates, and sulfides.
- 4. No attempt is made herein to develop a recommendation for the best binding agent to be used in all applications because more work is obviously required and such decisions would have to be made on a case-by-case basis. For example, authorities might select a more stable block in situations where currents were relatively low; whereas, a relatively fragile block (such as the Treatment E blocks of this study) might prove best in an area where the currents could disperse the scrap readily.

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THE IMPACT OF CRAB WASTES ON MARINE ENVIRONMENTS

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PART III

PROJECT REPORT

Part III.	The Impact of Crab Wastes on Marine Environments
Project No.	F19-82-00815
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Date:

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May, 1983

INTRODUCTION

The following paper constitutes the third and final portion of the completion report for the project entitled, "The Impact of Crab Wastes on Marine Environments." In this portion of the report efforts to determine if the growth of a potential fish pathogen, <u>Vibrio</u> <u>anguillarum</u>, is enhanced by crab scrap and to further characterize the affinity of crab scraps for cadmium are described (see Part I of Project Report).

METHODS AND MATERIALS

The Bacteriological Studies

As alluded to above, <u>Vibrio anguillarum</u> was selected for the experiments in which an attempt was made to demonstrate that the growth of bacterial fish pathogens might be promoted by crab scrap. <u>V.</u> <u>anguillarum</u> is widely recognized as an important fish pathogen, but little work has been performed with the bacterium. It occurs widely in both pathogenic and non-pathogenic forms and only through a rigorous testing protocol may it be determined whether or not a given isolate is pathogenic. The culture used in this study was originally isolated from a fish lesion, but the pathogenicity of the culture was not characterized. The culture was ordered from The American Type Culture Collection (ATCC) in Rockville, Maryland (ATCC No. el9264).

The <u>V. anguillarum</u> culture was maintained and enumerated on media 265, a medium recommended by ATCC personnel. The composition of media 265 is given below:

heart infusion broth	12 .5 g
nutrient broth	5.4 g
yeast extract	2.5 g
distilled water	1.0 L

In situations where it was necessary to use a hard agar base (e.g. in preparing slants or petri dishes) 23.5 g of nutrient agar was added to the above medium in lieu of 5.4 g of nutrient broth. The culture was routinely incubated at 23°C and enumerated by means of a spread plate technique.

The work performed with the <u>Vibrio</u> basically consisted of placing the organism in various types of systems and monitoring on a daily basis any changes in the microbial population. The eight types of systems considered are described in Table 1. As indicated in Table 1, crab scrap (1.5 g) and/or sediment (5.0 g) were (was) placed in test tubes along with a 2 percent sodium chloride solution or seawater (9 ml of fluid in each case). Each tube was then inoculated with <u>V. anguillarum</u> to provide a titer of about 100 organisms per ml. Each tube was incubated at 23°C and the levels of <u>Vibrio</u> in each of the tubes were assayed daily over a period of 42 days.

The Cadmium Adsorption Studies

Some adsorption studies with cadmium were performed previously and described in Part I of the final report. To enhance this data base additional experiments with cadmium were performed and are described herein. The procedure and materials for performing each series of experiments were very similar. In this phase of the work either 4 or 8

		Syst	em <u>Component</u>	
<u>System</u>	Crab Scrap	Sediment	2% Salt Solution*	Seawater
1	x	×		х
2		х		x
3	Х			х
4	Х	х	×	х
5	Х		×	
6		х	x	
7				x
8			x	

Table 1.	The types	of syst	tems co	nsidered	in	the
	bacterio	logical	studie	s.		

*Solution was prepared with distilled water and NaCl.

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gms of cleaned crab shell or ground crab scrap was continuously shaken for a period of 7 days in 200 ml of seawater which contained l mg/L of cadmium. A sample of the solution phase in each flask was taken each day for cadmium analysis, so that the amount of cadmium adsorbed to the crab materials could be determined. Each trial was performed in triplicate at room temperature $(23 \pm 1^{\circ}C)$.

RESULTS AND DISCUSSION

The Bacteriological Studies

As indicated earlier, the growth of <u>Vibrio anguillarum</u> was monitored in eight different systems. This experiment was designed so that the effects of sediment, crab scrap, and suspending fluid (2% salt solution vs. seawater) on growth of the <u>Vibrio</u> could be determined (see Table 1). The results of this work are presented in Figures 1 through 8.

Figures 1 through 3 illustrate the effects of sediment and crab scrap on the growth of the <u>Vibrio</u> in seawater. Growth data for <u>Vibrio</u> in seawater alone are presented in Figure 7. These data readily demonstrate that the growth of the <u>Vibrio</u> was greatly enhanced by the presence of crab scrap. Note that the ordinates of Figures 1 and 3 are labeled in terms of hundreds of millions, as opposed to a label of hundreds of thousands in Figures 2 and 7. The organism therefore grew very little in seawater alone, but reproduced somewhat (to levels of 1-4 x 10^5 organisms/m1) in the presence of sediment and reached very high levels (1-8 x 10^8 organisms/m1) in environments containing crab scrap.

















Sediment appeared to enhance the growth and viability period of the organism in the presence of crab scraps.

The data obtained when the suspending medium was a 2.0 percent salt solution were similar to the results derived from the trials conducted with seawater. Figures 4 through 6 show how sediment and crab scrap influenced the growth of the Vibrio in the salt solution, whereas Figure 8 illustrates how the organism reproduced in the salt solution alone. As before, it was necessary to construct the graphs using different multipliers on the ordinate axes. Figures 4 and 5 were plotted using values in the hundreds of millions, while Figures 6 and 8 were constructed using a multiplying factor of hundred thousands. As noted in the seawater trials, crab scrap was principally responsible for promoting the growth of the Vibrio, and the sediment appeared to enhance growth somewhat as well as permit the population of organisms to remain at a high level for a more extended period. No firm statement may be made about the relative abilities of the two suspending fluids (salt solution vs. seawater) to support the growth of the Vibrio, but it does not appear that there was any appreciable difference.

The Cadmium Adsorption Studies

The results of the cadmium adsorption studies are presented in Figures 9 through 12. Note that within about 4 to 5 days 4 and 8 grams of cleaned crab shells adsorbed approximately 70 and 90 percent, respectively, of the cadmium initially dissolved in the seawater (1 mg/L Cd). These results are fairly consistent with the data presented in Part I of the final report. In experiments with ground crab scrap (see















Cadmium uptake in flasks containing 8 grams of ground scrap and 200 ml seawater. The initial concentration of Cd⁺⁺ was 1 ppm. Figure 12.

Figures 11 and 12) it was discovered that the scrap again readily adsorbed cadmium, but the uptake of the metal was less consistent. Organic matter associated with the scrap may have interfered with the sorption of the metal on the shell by competing for shell adsorption sites and/or sorbing the metal itself. It is also possible that variations in the data were noted because organic materials suspended in the test flasks interfered with the means of detecting the metal, atomic absorption; i.e., the materials tended to clog the sample nebulizer.

CONCLUSIONS

In conclusion, the work in this phase of the project made two important statements:

- There is an indication that crab scraps may promote the growth of bacterial fish pathogens. Certainly, the growth of <u>Vibrio</u> <u>anguillarum</u> was enhanced in this study by the addition of crab scraps.
- Crab scraps have an affinity for cadmium which suggests that the scraps may also adsorb other metals.

Both of the above conclusions need to be carefully factored into the processes of selecting and managing an ocean disposal site for crab scraps.