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DOE/PC/92521--T173

TECHNICAL REPORT
March 1 through May 31, 1994

Project Title: **PLANT RESPONSE TO FBC WASTE-COAL SLURRY SOLID MIXTURES**

DOE Grant Number: DE-FC22-92PC92521 (Year 2)
ICCI Project Number: 93-1/4.4A-1M
Principal Investigator: Robert G. Darmody, University of Illinois
Other Investigators: R.E. Dunker, Department of Agronomy, University of Illinois, and G.B. Dreher, W.R. Roy, and J.D. Steel, Illinois State Geological Survey
Project Manager: Dr. Daniel D. Banerjee, Illinois Clean Coal Institute

ABSTRACT

The goal of this project is to test the feasibility of stabilizing coal slurry solids (CSS) wastes by directly seeding plants into the waste. This is not done conventionally because the waste can generate toxic amounts of sulfuric acid. Our approach is to neutralize the potential acidity by mixing fluidized bed combustion (FBC) waste into the slurry. If successful, this approach would both help dispose of FBC wastes while providing a more economical slurry stabilization technique. The project involves growing forage plants in CSS-FBC mixtures in the greenhouse.

In the first two quarters we designed the experiment, secured greenhouse space, purchased the seeds, collected, dried, analyzed the FBC and CSS samples. The samples represent a typical range of properties. We retrieved two FBC and two CSS samples. One CSS sample had a relatively high $CaCO_3$ content relative to the pyrite content and required no FBC to neutralize the potential acidity. The other CSS sample required from 4.2 to 2.7% FBC material to neutralize its potential acidity.

This report covers the third quarter of the project. We produced the CSS-FBC mixtures, analyzed the soil fertility parameters of the mixtures, planted the crops, and monitored their growth. All mixtures support at least some plant growth, although some plants did better than others. It is too early to analyze the results statistically.

Next quarter the plants will be harvested, yields calculated, mineral uptake evaluated, and a final report will be written on plant response to CSS-FBC mixtures.

EXECUTIVE SUMMARY

The fluidized bed combustion (FBC) of high-sulfur coal is an attractive method for using Illinois coal, and FBC facilities are expected to become more numerous. When that occurs, the amount of waste generated by FBC operations will increase. Waste from FBC typically consists of 10-30% anhydrite and 25-45% calcium oxide or hydroxide. These wastes can have strongly alkaline pH values (12 or higher) when mixed with water. Typically, a limestone-water mixture will have a solution pH of about 8.

Another waste, coal slurry solids (CSS) from preparation of coal for combustion, consists of fine-sized coal particles and clays. The coarser coal particles often have pyrite associated with them. This fine particulate fraction is discharged in a water stream to a slurry pond, where the solids settle out and the water is recycled through the cleaning process. When the slurry pond reaches its solids-holding capacity, the pond is no longer used and must be reclaimed by an acceptable method. If the pyrite in the coal is allowed to oxidize, it produces acid. Acidic conditions preclude plant growth. Operators cover filled slurry ponds with four feet of soil to prevent acid generation and allow plant growth. This an effective but costly means to stabilize the ponds.

In a previously funded ICCI project, FBC waste was shown to act as a neutralizing or buffering agent toward the potential acidity of CSS. This research is a follow-up on the initial study. It involves a greenhouse study to test plant response to FBC-CSS mixtures. If plants will grow in these mixtures, the expense of capping CSS ponds with soil may be eliminated.

The research should lead to subsequent field trials to test the feasibility of a more cost-effective slurry pond reclamation technique utilizing FBC waste.

Two FBC wastes and two CSS materials were collected from Illinois sources. The samples were air-dried, analyzed, then mixed in proportions to neutralize potential acidity. One of the two CSS samples had sufficient $CaCO_3$ to neutralize the potential acidity. The other sample required 4.2% of one of the FBC materials and 2.7% of the other FBC materials to neutralize its potential acidity.

After two weeks of weathering, the pH of the mixtures was within acceptable limits. This indicates that the acid generation potential of the CSS was mitigated by the FBC material.

Birdsfoot trefoil, tall fescue, and sweet clover were planted in the mixtures. The experimental design was changed to a randomized complete block from a completely randomized design

to remove position effects caused by differential heating and lighting in the greenhouse.

Plants have germinated and are growing in most of the pots. Fescue is growing the best and birdsfoot trefoil shows the worst growth. There appears to be some effect of the different mixtures on plant growth. Plant growth on one of the mixtures exceeds that on the other mixtures.

The effects of drainage conditions are inconclusive at this early stage.

In summary: 1. The FBC material prevents acidic conditions from developing in the weathered CSS material, 2. Plants will grow in the greenhouse in the FBC-CSS mixtures.

OBJECTIVES

The overall goal of the research project is to develop an environmentally acceptable method for using fluidized bed combustion (FBC) wastes in the reclamation of preparation plant coal slurry solids (CSS). The alkaline components of the FBC wastes will neutralize acid produced during the oxidation of pyrite contained in the CSS. The product may be a material that is suitable for plant growth after closure of the coal slurry pond. The specific goal of this project is a greenhouse study to determine the suitability of various plants for growth in the FBC-CSS mixtures.

INTRODUCTION AND BACKGROUND

As the use of fluidized bed combustion of Illinois high-sulfur coal increases, the amount of solid waste generated by those combustors will also increase. There will be concomitant concern over the disposal or utilization of the wastes. One potential beneficial use of the alkaline, calcareous waste is as an ameliorant to coal preparation plant slurry solids. This research could provide a method for using FBC waste in a way that benefits both the combustor operators and the coal mining companies.

Fluidized bed combustion allows the combustion of Illinois high-sulfur coal by trapping evolved SO_2 in pulverized limestone that is injected into the combustor with the pulverized feed coal. The process encourages the use of both Illinois coal and Illinois limestone, thus benefitting the economy of the State.

Pyrite in run-of-mine coal is partially removed from the coal during the cleaning process. Fine particles of pyrite become concentrated in the fine solids that are rejected from the cleaning process as a slurry. The slurry is usually discharged to a slurry pond where the solids settle out and the water is drained off and recycled through the process. When the slurry pond has reached capacity, or is no longer used, it must be dewatered and revegetated.

The hypothesis to be tested in the overall project is that coal slurry solids can be suitably amended by FBC waste so that the slurry solids will support plant growth either without the necessity of a four-foot thick soil cover, or with only a thin soil cover. If the hypothesis is true, and the method meets with regulatory acceptance, then the envisioned procedure can save mining companies the substantial cost of providing a soil cover on a closed slurry pond. For example, at $1.55/yd^3$, it would cost nearly $800,000 to cover an 80-acre slurry pond with four feet of soil. It will also provide a beneficial outlet for FBC waste while lessening or eliminating the problems associated with producing the material necessary for the four foot cover.

EXPERIMENTAL PROCEDURES

There will be three tasks in the research project:

1. Collect FBC wastes from two selected sites to give a representative wide range of FBC compositions. Combine the FBC and CSS samples to make four FBC-CSS mixtures designed to neutralize potential acidity.

2. Grow tall fescue, sweet clover, and birdsfoot trefoil in the FBC-CSS mixtures in the greenhouse. Measure plant growth and elemental composition of plant tissues.

3. Determine the effects of the various mixtures on plant properties to aid in the design of subsequent research.

Description of Experiments to be Performed

Task 1. Production of the FBC-CSS mixtures. The materials will be collected, analyzed, and mixed in the proper ratio to preclude acid generation. Samples from two FBC sites will be retrieved in plastic buckets. Sites were chosen based upon access and expected FBC composition to give a range in properties. Two CSS sites were selected for retrieval of material with a range in pyrite content to represent typical CSS properties. The CSS samples will originate from both major Illinois coal seams, #5 and #6. The materials from each site will be mixed and analyzed to determine composition. Table 2 gives the methods of analysis. Based upon measured properties, the CSS and FBC will be mixed to form four potential acidity controlled mixtures.

Task 2. Growing plants in FBC-CSS mixtures. The plants will be grown in 23-cm diameter pots on benches to be constructed in the greenhouse. The FBC-CSS mixtures will be analyzed by an independent soil testing lab to determine nitrogen, phosphorus, and potassium additions necessary to bring the fertility up to levels necessary to produce optimum yields. Total soluble salts will also be measured before and after the experiment to determine if it will have an impact on plant growth.

Three plant species will be grown individually in the mixtures, tall fescue, sweet clover, and birdsfoot trefoil. They are a grass and two legumes respectively. All are well known to be tolerant of a wide range of salt and pH conditions similar to those expected in the mixtures. In addition, these three plant species are tolerant of Illinois conditions, and a mixture of them would most likely be used in any field application of this research. A mixture of grasses and legumes is typically grown where a low maintenance plant cover is desired because the legumes provide nitrogen for the grasses which are better at protecting the surface from wind and water erosion.

The experimental design will be completely randomized with six replications. Three plant species, two FBC samples, two CSS samples, two drainage conditions, and six replications gives a total of 144 pots. The experiment will include two sets of pots. One set will be sealed on the bottom to simulate closed drainage field conditions. The other set will be in pots with drain holes in the bottom. These will simulate freely drained field conditions. The pots will be maintained in a moist condition by watering them with deionized water. Water contents will be monitored by weighing the pots every other day.

Task 3. Plant response to FBC-CSS mixtures. Seeds will be counted to represent typical field seeding rates and hand placed in each pot. Germination success will be recorded. After 6-8 weeks, all the above-ground portions of each plant will be harvested, weighed, dried, and weighed again to determine moisture content and dry matter production. The tissue samples will be sent to an independent forage analysis lab to determine quality and minor elemental composition.

Data Interpretation

The data from the experiment will be statistically analyzed using a completely random design and statistical software on a personal computer. There will be two CSS materials, two FBC materials, three plant species, and six replications. The major products of the research will be data indicating design considerations and the probability of success in direct seeding of FBC amended coal slurry ponds.

RESULTS AND DISCUSSION

Work to date includes securing greenhouse space, purchasing plant seeds, and collection, cataloging, and drying the research materials. We have also developed the CSS-FBC mixtures and planted the crops. The crops have germinated and the tallest ones are now approaching 25 cm.

Task 1 has been completed and task 2 is well underway. Task three has been initiated. Plans for next quarter involve completion of tasks 2 and 3.

Because lighting and cooling varied in the greenhouse, the experimental design was changed from a completely randomized design to a randomized complete block. This change will allow us to remove the effects of position from the research results.

Analyses of initial pH, cation exchange capacity (CEC), and plant nutrients in the CSS-FBC mixtures have been completed (Table 1). The mixtures were found to be high in P and K. The mixtures were also analyzed for total content of selected constituent elements (Table 2).

Each individual pot was analyzed for pH after 2 weeks of simulated weathering in the greenhouse. Comparison of these values (Table 3) to the initial values of the fresh mixtures shows the effectiveness of the FBC amendment in balancing the pH of these systems, at least for the short term. The pH of the mixtures will be determined again at the end of the greenhouse experiment to see if the pH has remained near neutral.

The particle size distributions (Table 4) and soil moisture release characteristics of the CSS materials and the CSS-FBC mixtures have also been determined (Table 5). The mixtures are a coarse sandy loam and show typical soil moisture release characteristics.

The greenhouse phase of the experiment is nearing completion, with sweet clover and tall fescue growing satisfactorily on the mixtures. Birdsfoot trefoil (BFT) lags in emergence and growth. Because the plants have not been harvested, we can provide only a subjective and inexact evaluation of the plant response to the mixtures. Most pots seeded to BFT failed to sustain more than two plants out of 20 seeds planted. About half of the pots seeded to sweet clover have sustained three or more plants, with the Crown CSS (C) sustaining more plants than Turris/Geon (TG) and Turris/MWG (TM). All of the pots seeded to tall fescue produced and have sustained at least 6 plants. One pot of sweet clover was barren. This was a poorly drained pot of the TG mix. There were seventeen pots which didn't contain any living plants after 42 days. Most of these pots were the TG mixture.

Potassium deficiency symptoms were observed on the sweet clover growing on the C material after 18 days. Later, the occurrence of these symptoms increased and showed up on sweet clover growing in the TM mix as well. Additional K fertilizer was added and apparently corrected the problem. 25 days into

Table 1. Means (CV %) of soil fertility for CSS-FBC mixes.

Analysis	C	T G	T M
pH	5.6 ± 2.2	8.8 ± 5.0	9.2 ± 3.7
CEC(meq/100g)	96.0 ± 6.7	50.0 ± 1.5	42.8 ± 8.8
Soluble S(ppm)	4218.0 ± 10.6	6129.0 ± 3.6	5537.0 ± 14.6
Easily Extract. P			
lb. P2O5/A	38.0 ± 28.9	29.0 ± 6.9	32.0 ± 12.5
ppm	8.0 ± 25.0	6.0 ± 0.0	7.0 ± 14.3
Bray II P			
lb. P2O5/A	91.0 ± 35.2	101.0 ± 5.0	152.0 ± 7.9
ppm	20.0 ± 35.0	22.0 ± 4.5	33.0 ± 9.1
Ca			
lb./A	24130.0 ± 9.2	16901.0 ± 1.3	14098.0 ± 9.6
ppm	12065.0 ± 9.2	8451.0 ± 1.3	7049.0 ± 9.6
Mg			
lb./A	370.0 ± 2.4	1051.0 ± 3.1	1044.0 ± 4.4
ppm	185.0 ± 2.7	525.0 ± 3.2	522.0 ± 4.4
K			
lb./A	200.0 ± 8.0	272.0 ± 0.7	290.0 ± 6.6
ppm	100.0 ± 8.0	136.0 ± 0.7	145.0 ± 6.9
Na			
lb./A	636.0 ± 10.5	808.0 ± 2.5	874.0 ± 8.2
ppm	318.0 ± 10.4	404.0 ± 2.5	437.0 ± 8.2
%Base Saturation			
Ca	62.8 ± 5.8	84.4 ± 0.7	82.3 ± 1.1
Mg	1.6 ± 5.6	8.7 ± 2.2	10.2 ± 5.9
K	0.3 ± 11.1	0.7 ± 1.1	0.9 ± 8.0
Na	1.5 ± 15.2	3.5 ± 3.5	4.5 ± 9.2
Other Bases	6.2 ± 3.7	2.6 ± 17.0	2.2 ± 15.5
H	27.6 ± 12.7	0.0 ±	0.0 ±
Extractable minors (ppm)			
B	1.9 ± 1.6	22.8 ± 3.6	8.6 ± 3.0
Fe	1208.0 ± 14.6	1805.0 ± 6.4	1562.0 ± 5.1
Mn	110.0 ± 8.2	89.0 ± 1.1	91.0 ± 4.4
Cu	1.3 ± 9.3	0.9 ± 2.4	1.3 ± 7.8
Zn	5.5 ± 15.8	6.7 ± 6.6	4.0 ± 8.8
Al	28.0 ± 67.9	200.0 ± 7.0	120.0 ± 34.2

Table 2. Total content of selected elements in CSS-FBC mixtures.

	Mixture					
	C		T G		T M	
	Mean	CV(%)	Mean	CV(%)	Mean	CV(%)
Element	ppm					
Al	52,082 ±	10	45,858 ±	9	4 ±	7
B	1,135 ±	4	1,126 ±	5	1,210 ±	6
Ba	365 ±	15	470 ±	14	421 ±	27
Ca	92,432 ±	5	90,812 ±	5	92,442 ±	7
Cd	24 ±	15	27 ±	14	29 ±	7
Cr	41 ±	18	43 ±	19	50 ±	30
Co	32 ±	9	42 ±	4	46 ±	3
Cu	55 ±	14	61 ±	10	67 ±	12
Fe	79,127 ±	13	107,977 ±	4	117,406 ±	6
K	6,450 ±	5	7,816 ±	8	8,241 ±	9
Mg	10,395 ±	10	11,915 ±	7	13,644 ±	6
Mn	894 ±	4	752 ±	1	819 ±	7
Na	2,730 ±	9	3,526 ±	8	3,571 ±	15
Ni	54 ±	13	58 ±	16	81 ±	49
Pb	54 ±	7	61 ±	12	71 ±	8
S	97,567 ±	13	125,956 ±	6	139,596 ±	7
Zn	891 ±	46	421 ±	73	589 ±	45
	ppb					
As	9,994 ±	45	37,050 ±	4	35,350 ±	6
Hg	173 ±	7	254 ±	12	522 ±	118
Se	2,256 ±	10	2,154 ±	10	1,492 ±	45

Table 3. pH of mixes after weathering.

MIX	pH	STD
G	7.5	0.3 a
M	7.5	0.1 a
C	7.2	0.2 b
REP		
6	7.5	0.2 a
5	7.5	0.2 a
3	7.5	0.2 a
2	7.4	0.2 a
4	7.4	0.2 ab
1	7.3	0.3 b

Note: Values in the same group with the same letter are not significantly different (.05).

Table 4. Texture of CSS-FBC mixes.

Size Separate	C	T	TG	TM
	----------%--------			
Sand	69	67	76	73
VCos	8	10	11	11
CoS	19	16	18	18
MS	19	17	20	19
FS	17	18	20	19
VFS	6	6	7	6
Silt	21	21	17	18
Clay	10	12	7	9
Class*	CoSI	CoSL	CoSL	CoSL

* USDA textural class

Table 5. Moisture release dynamics of CSS-FBC mixtures.

Pressur (bar)	Mixture			
	C	T	TG	TM
	----Wt.% Moisture----			
0.1	22.8	19.6	24.4	24.8
0.33	16.1	14.2	17.8	16.7
1	12.2	11.1	9.0	13.0
5	9.6	9.1	9.8	9.8
10	8.1	8.6	9.6	9.2
15	7.9	8.1	9.0	8.8

the experiment, a malformation of the younger leaves was noted on some sweet clover plants growing on TG and TM mixes. Later it showed up on the C mix as well. This seems to be a symptom of a deficiency or toxicity of some element, but it will not be positively identified until we analyze the plant material after harvest.

CONCLUSION AND RECOMMENDATIONS

Analytical results indicate a wide range in chemical composition of the materials. Thus it is recommended that any work involving these types of materials include thorough chemical and physical characterization.

Plants are growing on all of the mixtures. Fescue exhibits the most growth and birdsfoot trefoil shows the least. Some pots are barren due to poor or no seed germination. One mixture appears to be superior in plant growth response. The effect of drainage on plant growth is variable and will have to be determined statistically.

PROJECT MANAGEMENT REPORT
March 1 through May 31, 1994

Project Title: **PLANT RESPONSE TO FBC WASTE-COAL SLURRY SOLID MIXTURES**

DOE Grant Number:	DE-FC22-92PC92521 (Year 2)
ICCI Project Number:	93-1/4.4A-1M
Principal Investigator:	Robert G. Darmody, University of Illinois
Other Investigators:	R.E. Dunker, Department of Agronomy, University of Illinois, and G.B. Dreher, W.R. Roy, and J.D. Steel, Illinois State Geological Survey
Project Manager:	Dr. Daniel D. Banerjee, Illinois Clean Coal Institute

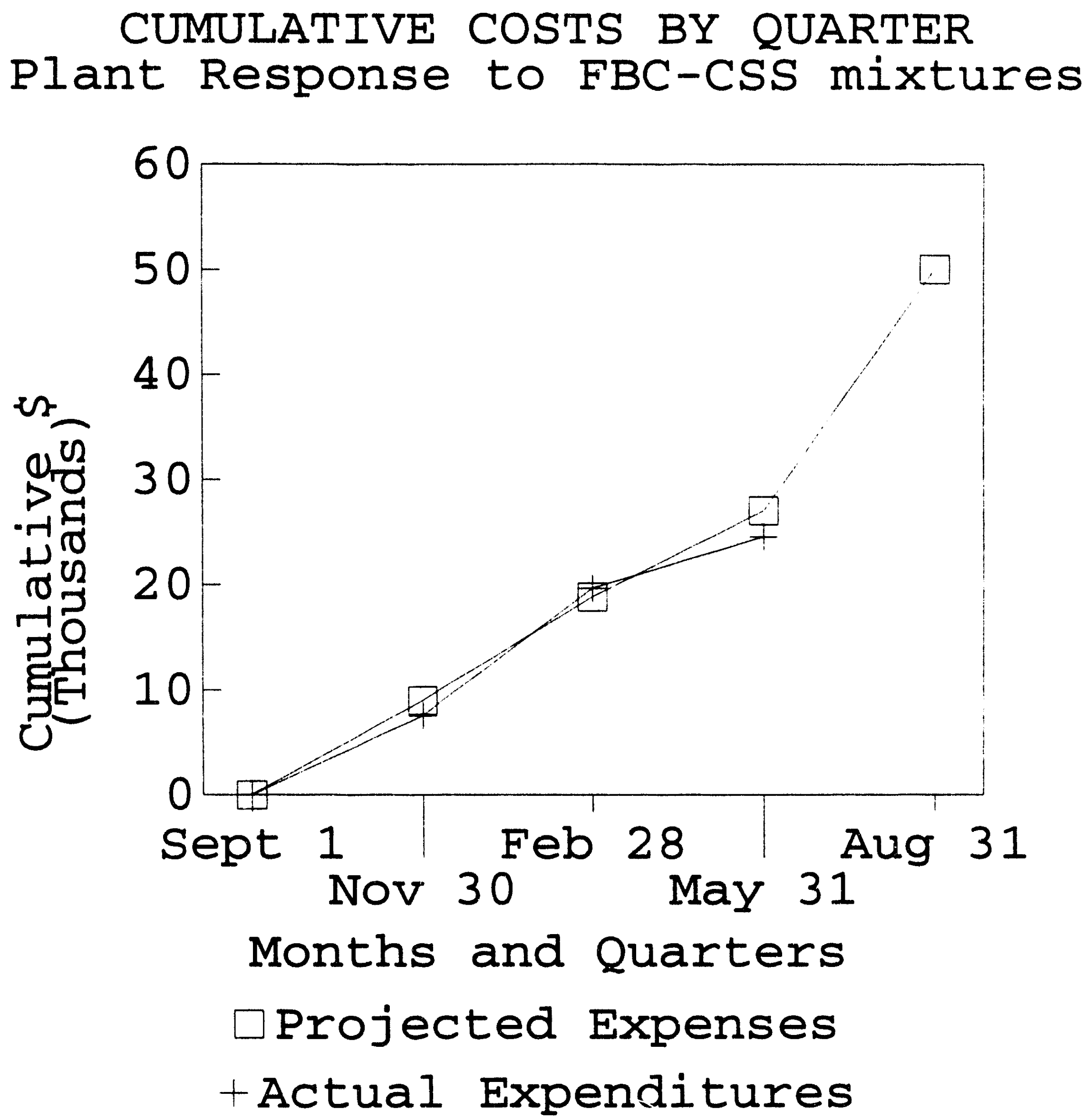
COMMENTS

There were no significant deviations from the proposal budget with the exception of a request to purchase a laboratory balance. Everything is going essentially as planned however the account for the project was not setup on time and consequently we could not start the project on time. In addition, the CSS material was much more slow to dry than anticipated. The cool weather delayed germination and variable conditions in the greenhouse required us to reorganize the experimental design. Consequently, we are somewhat behind schedule.

CUMULATIVE PROJECTED AND ESTIMATED EXPENDITURES BY QUARTER

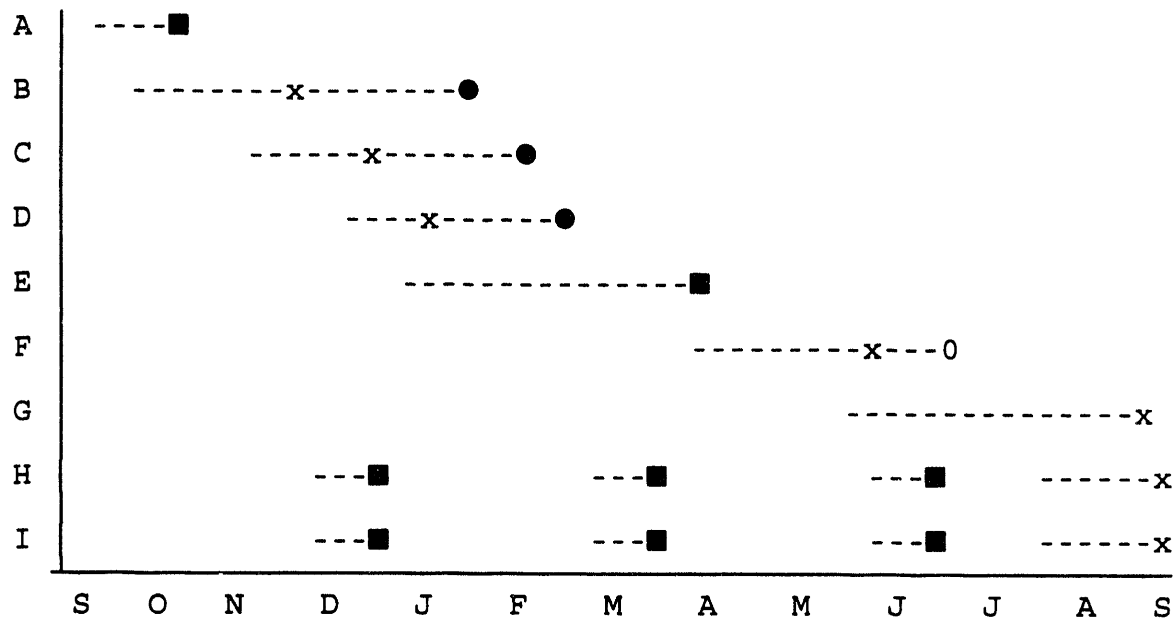
Quarter *	Types of Cost	Direct Labor	Fringe Benefits	Materials & Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Costs	Total
Sept. 1, 1993 to Nov. 30, 1993	Projected	3,675	368	100	150	0	3,460	775	8,528
	Estimated	6,119	1,208	0	141	0	60	20	7,548
Sept. 1, 1993 to Feb. 28, 1994	Projected	8,573	857	200	160	0	6,920	1,671	18,381
	Estimated	13,950	2,819	158	141	0	798	1,787	19,653
Sept. 1, 1993 to May. 31, 1994	Projected	15,071	1,658	300	175	980	6,920	2,510	27,614
	Estimated	16,528	3,275	202	141	980	1,150	3,230	25,506
Sept. 1, 1993 to Aug. 31, 1994	Projected	27,625	3,144	406	226	980	13,100	4,548	50,029
	Estimated								

*** Cumulative by Quarter**



Total ICCI Award $50,029

SCHEDULE OF PROJECT MILESTONES



Begin September 1, 1993

Milestones:

A. Collect FBC and CSS samples (Task 1)
B. Analyze FBC and CSS samples (Task 1)
C. Prepare FBC-CSS mixtures (Task 1)
D. Analyze FBC-CSS mixtures to determine fertility application (Task 2)
E. Setup greenhouse experiment and grow plants (Task 2)
F. Harvest plants and analyze constituents (Task 2)
G. Interpret data (Task 3)
H. Technical reports prepared and submitted
I. Project management reports prepared and submitted

Comments:

Late notification of an account number for the project caused a delay in starting the project.

DATE
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10/19/94

END