

# final report

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# Removing and Recycling of Proteins from the Waste Waters of abbatoirs using clay

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#### **EXECUTIVE SUMMARY**

Liquid effluent from Australian abattoirs is largely regarded as wastewater which is added to the environment, either directly eg. in sewers, or after either aerobic or anaerobic treatment, although some is used for irrigation. However, tightening regulations, a limited capacity of soils for the effluents and also high energy costs, especially for forced aeration, mean that new options are required for the treatment and disposal of abattoir liquid effluent. There is a particular need for the removal of nutrients from the effluent. Nitrogen causes a special concern as a source of high biological oxygen demand (BOD). Most organic nitrogen in the effluent is protein based. As well as posing an environmental hazard, the protein which is disposed of in effluent also represents a wasted economic resource and presents an opportunity for recycling.

Accordingly, a laboratory study was carried out to determine the extent of removal of proteins from abattoir wastewater by 10 different Australian clays, and also a clay from the USA. The effect of different environmental conditions upon the effectiveness of protein uptake by clays were determined. Methods for the extraction of clay-protein complexes from the waste waters were explored and the complexes were characterised for chemical and physical properties relevant to their possible reuse. Possible technologies for the application of the process to abattoirs were examined and the economic feasibility of the use of clays for the recycling of soluble abattoir effluent proteins was assessed.

Bentonite clays were the most effective for the removal of proteins. If sufficient clay was added (≥1% suspension), all of the protein could be removed from raw abattoir wastewater without any adjustment of conditions. The different bentonites varied in their efficiencies of uptake, but uptake could be improved by a decrease in pH. Bentonite structure had some effect on uptake, with proximity of charge to the surface of the layer favouring uptake, but ease of separation of clay layers had an important influence. All clays became saturated with protein at a sufficiently high concentration of the protein in solution. Provided sufficient clay was added, bentonite-protein complexes settled out of solution by flocculation within minutes, so that addition of coagulants was not necessary to help clear solutions.

Addition of clay reduced chemical oxygen demand (COD) of wastewater by >4 times. The clays were more effective for the reduction of total nitrogen than of phosphorus, either inorganic, or total, from wastewater.

The products of treatments of abattoir liquid effluent with bentonites had lower levels of nutrients than common animal feeds, but bentonite itself has been shown elsewhere to have benefits for animal health and nutrition. The clay-protein complexes from wastewater treatment would provide similar amounts of nitrogen and phosphorus as manures, and it is also suggested that they would assist in increasing water- and nutrient-holding capacities, especially of sandy soils. Although the products of clay-effluent interactions had some capacity to remove nonionic organic contaminants such as hydrocarbons, from water, their use would mean that the reduction of xenobiotic

contaminants ie. hydrocarbons would be at the expense of the addition of biologically active contaminants ie. proteins.

In an abattoir operation, it is envisaged that the process would follow a Dissolved Air Flotation (DAF) system, in order to minimise fat. Clay could be added into the wastewater flow as a powder or else as a slurry via a high shear, flow through mixer, or, in the case of the slurry, after the generation of turbulent flow. The complex could be recovered by settling into the base of a conical tank following slow circulation in the tank or recovered using hydrocyclone technology. The resulting sludge, after dewatering, could be rendered for drying and added to meatmeal. Alternatively, it could be composted along with solid abattoir wastes for the production of potting mix, where it would act as a slow release nitrogen fertiliser and add the benefit of the increased moisture-holding capacity of the clay.

The use of the clay-protein complex in potting mix provides the most economically viable application of the products. Economic feasibility is improved by the use of the process for treating only high COD waste streams, especially that from low temperature rendering operations. It is also improved by the use of a clay loading which maximises protein uptake per gram of clay ie. ~0.08% suspension. 58% of protein in wastewater can be removed with this particular clay loading. If it is assumed that the clay-protein product is added to the composting mixture at a concentration of 30%, and the composted product is sold, without packaging, as a bulk potting mix at \$35/tonne (a premium of \$5/tonne over that charged for common potting mixes), there would be a payback period of ~ 3.75 years and a maximum internal rate of return of ~22%. Savings on the requirements for, and costs of, waste disposal and treatment would also derive from the reduction of organic loads. The economic feasibility of the process may be further improved by pre-treatments designed to increase the capacity of the clays to bind proteins and by recycling the clay used.

The process for the removal of proteins from abattoir wastewater using clays requires trialling at a pilot scale, and the products should be tested as slow-release fertilisers in plant growth trials.

#### **PROJECT OBJECTIVES**

- 1. To determine the extent of uptake of proteins and related sources of nitrogen in abattoir wastewaters by different Australian clays under realistic condition s of eg. pH, concentrations, salt loadings, temperature and time.
- 2. To determine methods for the extraction of the clay-protein complexes from suspension.
- 3. To measure chemical and physical properties relevant to possible uses of the clay-protein complexes.
- 4. To consider how this technology would be applied in an abattoir.

5. To carry out an economic feasibility study evaluating the application of this process in an abattoir operation.

#### **CURRENT SITUATION**

The main methods used for the treatment and/or disposal of effluent wastewater from abattoirs in Australia are:

- 1. By irrigation
- 2. To sewers
- 3. In anaerobic lagoons
- 4. In anaerobic lagoons, including by forced aeration (McDonald, 1992).

However, all of these options have encountered problems in practice, including the overloading of both aerobic and anaerobic lagoons (Pitt and Skerman, 1992). It appears that irrigation, which is the principal final treatments option (Pitt and Skerman, 1992), has often been operating outside regulatory guidelines. In any case, many Australian soils are unsuitable for irrigation by wastewater containing nutrients and also salts (Green, 1992). Furthermore the capacity of soils for these wastes can be exceeded, so that deterioration of the soils and vegetation growing on them occurs and/or nutrients are leached through the soil profile, leading to a deterioration in the quality of ground water. Regulations are certain to prevent the disposal of untreated waste water into sewers where this still occurs.

In addition, treatment options can be expensive, as in the case of forced aeration, which incurs considerable energy costs. Principally, however, it is environmental considerations, reflected in tightening regulations, which are causing a re-examination of the present options and a need for new approaches for the treatment and disposal of effluent, including wastewater, from abattoirs (Johns and Greenfield, 1992b)

In particular, there is an increasing imperative for the minimisation of nutrients in wastewater from abattoirs (Johns and Greenfield, 1992b; Meat Research Corporation 1995). There is a particular concern over the disposal of nitrogen, and also phosphorus, into the environment. One of the major aims of this project was to use clays to bring about a reduction in the amount of nitrogen in wastewater released from abattoirs. Clays are a relatively cheap, widely available resource with a known attraction for proteins and which themselves have a benign effect on the environment.

Most of the organic nitrogen in abattoir waste water occurs as protein (Johns and Greenfield, 1992a), and most of this effluent protein occurs as blood, so that the major source of nitrogen in wastewater is blood (Meat Research Corporation, 1995). In 1996, The MRC Co-products Key Program Business Plan (Meat Research Corporation, 1996) reported that about 28,000 tonnes of protein are produced in the form of blood stickwaters in Australian abattoirs each year, with more soluble blood protein available as well from wet rendering and other abattoir operations. If it is left in effluent, this blood protein adds considerably to the biological oxygen demand of the effluents.

The soluble protein lost in wastewater represents not only an environmental hazard, but also a wasted economic resource. If the soluble protein could be removed in a

activated sludge replaced up to 25% of the crude protein were successful. Together with the minimal estimates of the protein content in effluent, these conclusions indicate that the liquid effluent contains considerable amounts of a potentially useful and profitable resource. With clays themselves having a positive value for both the health of animals and also as an aid to digestion (Anon, 1993), addition of proteins recovered from the liquid effluent to animals in the form of clay-organic complexes appeared to be a useful means of providing food to animals in a digestible form which also confers health benefits, while removing potentially environmentally damaging materials from waste. However, the recent world-wide concern over bovine spongiform encephalopathy (BSE, or mad-cow disease) may invalidate the use of proteins from animal processing as food for ruminants, at least temporarily, while still enabling their use for poultry.

Nonetheless, there is an alternative possible use of clay-protein complexes as fertilisers for the provision of nitrogen in a relatively slow-release form. Furthermore, addition of clays to soils as fertilisers should improve physical properties of soils such as their water-holding capacities. This particular use of the products from this process was examined closely (see "Analysis of Findings and Observations"). Another alternative, innovative, use of the clay-protein products as sorbents for organic pollutants was also examined (see "Findings and Observations").

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#### RESEARCH METHODOLOGY

#### 1. General

Wastewater was obtained from an abattoir (Metro Meats International, at Murray Bridge, South Australia) whenever required for experiments. Visits had first been made to other abattoirs (Q Meat, Brisbane, to examine abattoir and wastewater operations, and Lobethal Abattoir Pty. Ltd., to examine waste water operations). It was then decided to obtain wastewater only following its treatment by dissolved air flotation (DAF), mainly in order to minimise the fat content in the samples. Metro Meats International at Murray Bridge provided the most easily accesible source of DAF-treated waste water among local abattoirs. For most experiments, the wastewater was first filtered using a coarse filter paper to remove solids. Samples were kept refrigerated between experiments and were usually disposed of and replenished with fresh samples after approximately 8-9 days.

Uptake experiments were conducted with 11 different clays. 7 of these were commercially-obtainable Australian bentonite or related smectitic clays, one was a commercially-obtainable bentonite from the USA (Volclay), while others were a

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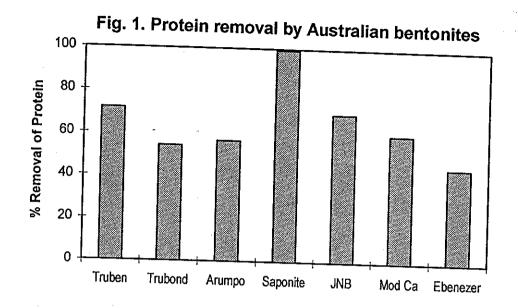
#### FINDINGS AND OBSERVATIONS

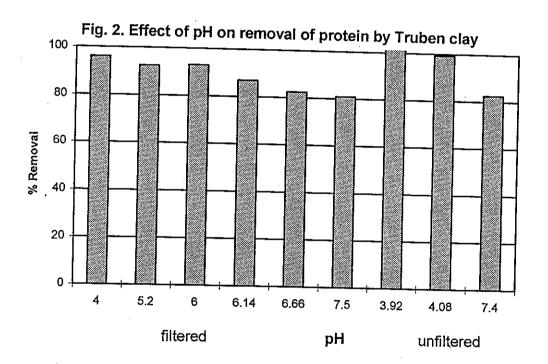
#### 1. Removal of protein using different clays

Fig. 1 gives the percentage of protein which was removed by clay applied to raw waste water solutions at a concentration of 1%. It shows that all of the Australian bentonites tested can remove proteins from abattoir effluent but that the extent of removal varies with the different clays. One particular Australian bentonite, Saponite, removed all of the protein at this rate of addition to effluent. Of the other clays, Volclay removed 83%, Keswick subsoil 27%, and the vermiculite and palygorskite each removed 25% as much protein as Saponite (data not shown in Fig.1). Most of the later experiments used only the Australian bentonites.

## 2. Effect of different factors on uptake and removal of proteins by clays

a. pH and filtering. Fig. 2 shows the effect of pH on the uptake of proteins by one of the bentonite samples from both filtered and unfiltered effluent. A decrease in pH led to an increase in percentage uptake of protein from both filtered and unfiltered effluent. This trend with pH is consistent with results for the uptake of pure proteins by clays and reflects an increasing positive charge on the proteins with decreasing pH. It was observed that complexes formed at pH  $\leq$  5.2 all flocculated. An apparently greater percentage uptake from unfiltered than filtered effluent could represent the removal of insoluble protein from the former, possibly by entrapment in flocs.





b. Clay properties. Table 1 shows the maximum capacity of the different Australian bentonites for uptake of protein from effluent as sampled in relation to a number of clay properties.

Table 1. Maximum capacity of Australian bentonites for effluent protein

		relation to	their	properties
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Sample	Max. protein uptake (mg/g)	CEC <sup>1</sup> (cmol(+)/kg)	рН	ESP <sup>2</sup> (%)	<2 μm (%)	Quartz (%)
Saponite	367.0	75.3	8.6	80	99	4
Ca modified	313.1	···· 81.4	10.4	72	69	15
Truben	246.0	56.6	5.1	54	79	11
Trubond	214.8	67.5	9.8	79	88	5
Ebenezer	209.7	69.0	10.3	83	69	9
JNB	205.5	53.0	5.0	36	50	16
Arumpo	114.0	86.3	5.1	51	64	3

cation exchange capacity (indicates negative charge) calculated for clay dried at 105°C

<sup>2</sup> Exchangeable sodium percentage (Na/CEC)

According to Table 1, the capacity of the different bentonites for effluent protein showed no clear relationship to total (negative) charge, as given by CEC. The bentonite with the highest charge (Arumpo) showed the lowest capacity for protein by a considerable margin, while the most effective bentonite for protein uptake (Saponite) had only an intermediate value for CEC. The highly sorbent Saponite also had the finest texture among the samples, and, along with the poorly sorbent Arumpo, the lowest proportion of quartz. Neither of these attributes can account for extent of protein uptake. Neither was there any consistent effect of pH on protein uptake.

Table 1 further indicates that all except Truben, JNB and Arumpo have high ESPs, ie.are highly sodic, a condition which normally promotes protein uptake. The percentage removal of protein from 25ml raw waste water by 0.02g of each bentonite, which is a lower amount than required for maximum removal of protein, was compared before and after bentonites had been exchanged with excess Na to make them all similarly highly sodic. The results are shown in Table 2.

Table 2. Effect of Na treatment on removal of protein by Australian

/			pentor	ntes		
Sample	Raw ben	tonites	Na-treate	d bentonites	Percentag	ge change
·	ESP	% removal	ESP	% removal	ESP	% removal
Saponite	80	55.9	90	49.5	+10	-11
Ca modified	73	55.8	88	38.5	+21	-31
Truben	54	38.2	88	52.3	+63	+37
Trubond	79	51.7	89	53.1	+13	+3
Ebenezer	83	41.3	93	41.6	+12	<+1
JNB1	49	34.5	91	52.1	+86	+48
JNB2	36	9.3	96	47.3	+167	+409
Arumpo Arumpo	51	8.3	92	10.2	+80	+23
ultrasonified	51	8.3	92	35.7	+80	+330

Table 2 shows that increases in exchangeable sodium had vastly different effects on the efficiencies of the different bentonites for protein removal. There was either no effect, or, in 2 cases, a negative effect, of increases in exchangeable sodium on bentonites with an initially high ESP (>~70). There were increases in the efficiencies of bentonites with low ESPs (<~55) when they were further treated with sodium ions. However, these increases in efficiencies ranged from only 23% for the Arumpo sample to over 400% for the JNB2 sample, even though they each had similar initial ESP values. While degree of sodium exchange affects the affinities of the bentonites for protein, there appears to be a maximum degree of sodium saturation beyond which no effect is shown and, also, there are other influences on uptake besides degree of sodium exchange. In the case of the Arumpo bentonite, for which Na exchange does not promote complete swelling and dispersion, according to earlier studies (unpublished results, Absorbent Clay Project, CSIRO Division of Soils, 1994-1996), ultrasonication greatly improved protein uptake, confirming the effect of increased separation of layers upon ease of uptake of proteins.

While there was no clear relationship between the total charge of each clay and protein uptake, the possibility that the location of the charge within the aluminosilicate clay mineral affected the uptake was investigated. The structure of the smectite clays which constitute bentonites are represented in Figure 3. The charge on these clays derives almost entirely as a result of the substitution of either trivalent Al by divalent Mg, thereby providing net negative charge in the octahedral Al-rich sheets sandwiched between two tetrahedral Si-rich sheets in the aluminosilicate layers and/or by the substitution of quadrivalent Si by trivalent Al within the tetrahedral layers themselves (Fig. 3). Regardless of the point of origin of the charge, it is largely expressed between the layers, within in the interlayer region of the minerals. Proteins are adsorbed by the minerals because the proteins, which are positively charged through their nitrogen-based amino groups, are attracted electrostatically to the negative charges on the clay layers, as shown schematically in Figure 4. However, since charge based in the tetrahedral layers is located closer to the interlayer region than that based in the octahedral layers, it is possible that it would have more effect on the reactivity of the layers towards proteins than that derived from the octahedral layers. In Table 3, the tetrahedral contribution towards the total charge (CEC) is compared with the maximum protein uptake by raw clay from waste water which had a high protein uptake, with uptake on the same amount of raw clay from waste water with a lower protein content, and also with uptake from the same, lower proteincontaining waste water by clays following sodium exchange, to give the materials described in Table 2.

Fig. 3. Structure of smectite clays. Sheets of Al and OH hydroxides are sandwiched between those of Si and Al oxides in layers stacked parallel to other layers. The charge arises from substitution of ions by those of different valencies. It is balanced by hydrated cations in the interlayers.

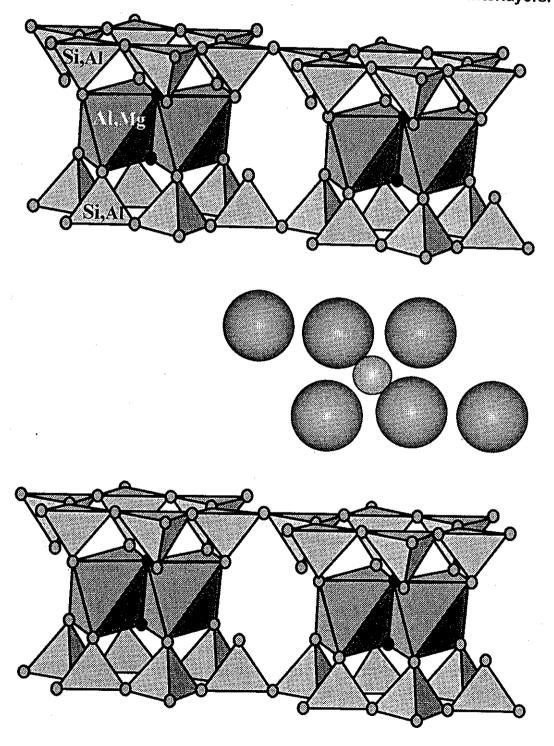
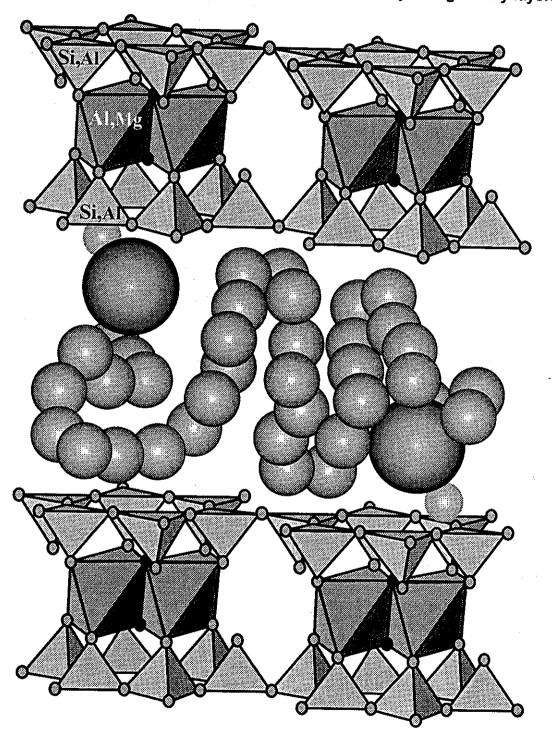


Fig. 4. Schematic diagram showing attachment of a protein molecule to a smectite clay within the clay interlayers by means of the attraction between the positively-charged amino group, centred on nitrogen (represented by large spheres) and the negatively-charged clay layers



According to Table 3, high uptake of protein by the raw clays tended to occur when tetrahedral contribution to the total charge was high ie. for the Saponite and Modified Ca clays, and there was a corresponding low uptake when the tetrahedral contribution was low ie. for Arumpo clay. However, the relationship is by no means clear-cut. Furthermore, it no longer dominates when uptake from Na-exchanged clays is considered. The different uptake values are plotted against tetrahedrally-derived charge in Fig. 5.

Table 3. Protein uptake in relation to contribution of tetrahedral charge to CFC

Clay	YY	ECD	OFC		OLO	<del></del>		
Clay	pН	ESP	CEC cmol/kg	% Tet. charge	CEC (Tet.) cmol/kg	Uptake mg/g raw clay (High protein)	Uptake mg/g raw clay (Low protein)	Uptake mg/g Na- clay (Low protein)
Saponite	8.6	80	75	100	75	367	162	144
Mod. Ca	10.4	72	81	34	28	313	162	112
Ebenezer	10.3	83	68	35	24	142	120	121
JNB2	4.3	30	39	46	18	n.d.	27	137
Trubond	9.8	79	62	25	16	210	150	154
JNB1	. 5	36	53	28	15	165	100	151
Truben	5.1	54	57	23	13	246	111	152
Arumpo	5.1	51	86	3	3	82	24	103

<sup>\* +</sup> ultrasonication for Arumpo

Together with Table 3, Fig. 5 shows that, while tetrahedral charge may have some influence on protein uptake, other factors are also influential. There is a general trend towards increasing protein uptake by the raw bentonites as tetrahedral charge increased, however, there were many exceptions to this trend. In particular, uptake by JNB2 was especially low, while that by JNB1 was also lower than expected from a smooth trend. On the other hand, when uptake by Na-clays was compared, there were smaller differences between all clays in efficiencies of uptake. It is noteworthy that Truben, Trubond, JNB1 and JNB2, which all came from the same locality (near Miles, in Queensland), each showed similar extents of uptake when sodiumexchanged. The much lower total charge of the JNB2 sample resulted in only a slight decrease in uptake when compared for those of these other three clays, again confirming that total charge does not explain differences well. This was again confirmed by the low uptake for the Arumpo bentonite, even after dispersion was enhanced by ultrasonication following sodium treatment. Nonetheless, sodium treatment, which enhanced uptake by the formerly less sodic samples (JNB2, JNB1, Arumpo and Truben), clearly influenced protein uptake.

c. Mechanism of uptake of proteins by clays. Isotherms for the weight of protein adsorbed by clay in relation to the concentration of protein remaining in solution are shown in Fig. 6 for bentonite clays.

n.d. not determined

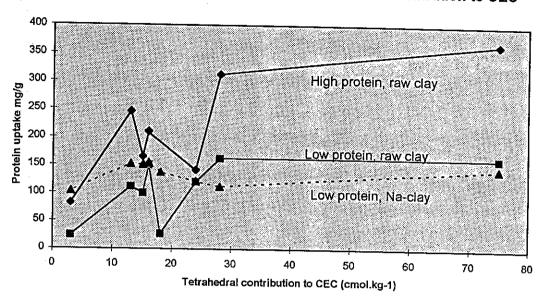
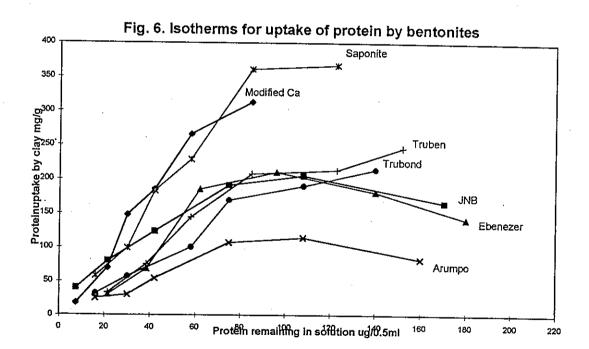


Fig. 5. Protein uptake in relation to tetrahedral contrbution to CEC



The shapes of the isotherms in Fig. 6 are consistent with the clays having a high affinity for the proteins up until the point at which their reactive sites become saturated with protein. The different clays have different total capacities for the proteins, although these may be changed by factors influencing dispersibility and ease of access of proteins to interlayer sites, especially degree of sodium-saturation, as already discussed. Apart from the effects of these factors, differences between the relative affinities of the different clays for proteins also alter with the concentration of protein remaining in solution, so that, for instance, JNB clay had a higher affinity for protein at concentrations below 20  $\mu$ g/0.5 ml (40 mg.L<sup>-1</sup>), while Saponite and the Modified Ca clays were much superior at higher concentrations.

## 3. Ease of removal of complexes from suspension and effect of removal on remaining wastewater

a. Determination of abilities of different clays to settle after protein uptake. Fig. 7 shows a plot of turbidity at different times after bentonite addition. Turbidity is measured in n.t.u.

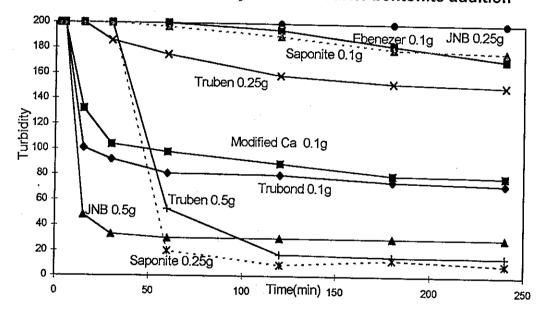


Fig. 7. Change in turbidity of effluent after bentonite addition

It was noted that, while some effluent treatments cleared rapidly, the effect was not always reflected by the turbidity readings, as the upper part of the loose flocs sometimes blocked the path of the beam. If this effect was ignored, on the basis of visual observations, all clays except one (Ebenezer) led to a relatively clear suspension within 20 min of addition. However, Saponite(0.25g) and Truben(0.5g) showed the greatest extent of clarification.

b. Clearing of clay-treated effluent with the aid of coagulants/flocculants. The results of these treatments, using clays and also with the effluent alone, are summarised in Table 4.

Table 4. Change in turbidity with time after clay addition with coagulants

Treatment	0.25g Sapo	nite added	0.5g Tru	ben added	0.5g Kesv	vick added
none	Turbidity 30min	Turbidity 4hr.	Turbidity 30min	Turbidity 4hr.	Turbidity 30min	Turbidity 4hr.
none	31	10.3	15	13.3	200	200
pH 3.5	47	10.4	80	4.7	102	21
FeCl <sub>3</sub> 40mg/L	189	137	200	85	200	200
FeCl <sub>3</sub> 100mg/L	5.8	2.9	200	146	200	200
Alum 40mg/L	94	66	200	200	200	200
0.1M NaCl	161	104	200	48	200	200
Poly 10mg/L	8	3.8	200	200	200	200
Poly 100mg/L	26	7.6	133	38	46	42

The only coagulant treatment which gave consistently lower turbidities than were obtained without the use of coagulants, except in one instance, was acidification (pH 3.5). It is noteworthy that the extent of protein removal, which was measured after each coagulation treatment, was 100% for all virtually all treatments of the Saponite and Truben clays but reached 100% for only the pH 3.5 treatment of the Keswick subsoil. In other cases, the subsoil removed between 50 and 60% of protein, except when used together with the high dose of the polyelectrolyte, when it was responsible for the removal of 80% of protein.

#### c. Effect of treatment of effluent with clay on Chemical Oxygen Demand COD

COD decreased from 4969 mg O<sub>2</sub>/ml in raw effluent to 1412 mg O<sub>2</sub>/ml in bentonite-treated effluent.

d. Effect of treatment of effluent on pH, ortho(PO4)-phosphorus total phosphorus, total Kjeldahl nitrogen, and total nitrogen, following coagulation.

Table 5. Concentrations of nutrients remaining in effluent after treatment with clays and coagulation

Clay*	Treatment	pН	Concentrat	ion remaining i concen		% of effluent
	·		PO <sub>4</sub> - P	Total P	TKN	Total N
Saponite	none	7.34	63	74	30	38
	pH 3.5	5.59	93	79	25	29
	FeCl <sub>3</sub> 40mg/L	7.27	94	67	35	33
	FeCl <sub>3</sub> 100mg/L	7.24	54	56	40	33
	Alum 40mg/L	7.25	88	68	20	29
	0.1M NaCl	7.4	100	76	30	29
	Poly 10mg/L	7.18	86	78	40	33
	Poly 100mg/L	7.62	75	74	25	29
Truben	none	6.81	77	58	30	33
	pH 3.5	3.9	100	79	25	24
	FeCl <sub>3</sub> 40mg/L	6.72	60	43	30	29
	FeCl <sub>3</sub> 100mg/L	6.67	29	38	33	33
	Alum 40mg/L	6.3	61	48	20	33
	0.1M NaCi	6.66	66	47	30	29
	Poly 10mg/L	6.75	73	52	25	33
•	Poly 100mg/L	6.99	70	64	40	39
Subsoil	none	6.74	100	79	60	62
	pH 3.5	4.38	80	74	25 ·	29
	FeCl <sub>3</sub> 40mg/L	7.0	72	80	65	67
	FeCl <sub>3</sub> 100mg/L	6.96	68	71	60	56
	Alum 40mg/L	6.94	87	78	60	57
	0.1M NaCl	7.24	100	77	60	52
	Poly 10mg/L	7.0	86	89	60	56
	Poly 100mg/L	7.17	84	66	30	33

<sup>\*</sup> Ratios Clay:effluent as for Table 1.

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Truben was more effective than either of the other bentonites for removing P. However, none of the clays effected the removal of very much phosphorus from the effluent, except when a high dose of ferric chloride was used with the Saponite and Truben clays, but not with the subsoil. Both Saponite and Truben removed significant

N.B. Coagulation treatments alone removed ≤ 50% N or P, most removed < 20%

N (generally > 60%). The subsoil removed a comparable amount of N only with the pH 3.5 and high polyelectrolyte treatments.

## 4. Characterisation of complexes for composition and structure and for animal food value and as environmental sorbents

Table 6. Elemental composition of the products of clay-effluent reactions

				I Cut	<b>, 110113</b>						
Sample	No	N	Ca	Fe	K	Mg %	Mn	Na	P	S	С
Saponite clay (Sap)		0.05	0.42	1.13	0.22	12.9	0.04	2.43	<.01	0.23	0.28
Sap-effluent mixture	1	2.98	1.55	0.74	<.05	5.35	0.02	0.12	0.21	0.22	n.d.
Sap-effluent complex	2a	1.51	0.78	1.04	<.05	11.2	0.04	0.83	0.13	0.17	12.25
44	2ь	1.51	0.78	1.10	<.05	11.9	0.04	0.20	0.09	0.11	10.82
" ,	2c	1.57	0.83	1.10	<.05	12.1	0.04	0.35	0.11	0.11	12.07
Truben clay (Tru)		0.01	0.04	0.4	0.06	0.37	<.01	0.54	<.01	0.03	0.33
Tru-effluent mixture	1	2.80	1.34	0.38	<.05	0.34	<.01	0.10	0.21	0.20	n.d.
Tru-effluent complex	2a	0.86	0.28	0.38	<.05	0.40	<.01	0.50	0.10	0.09	6.41
66	2b	0.90	0.30	0.36	<.05	0.39	<.01	0.23	0.07	0.06	6.71
64	2c	0.93	0.32	0.41	<.05	0.40	<.01	0.29	0.08	0.07	7.68
JNB clay (JNB)		0.01	0.33	0.28	0.06	0.26	<.01	0.10	<.01	0.12	0.16
JNB-effluent complex	2a	0.87	0.55	0.26	<.05	0.26	<.01	0.28	0.08	0.13	6.88
	2b	0.83	0.47	0.3	0.13	0.28	<.01	0.15	0.05	0.07	6.55
	2c	0.83	0.49	0.31	0.13	0.28	<.01	0.21	0.05	0.07	6.43

Indicates method of preparation (see above) Total N n.d. not determined

According to Table 6, addition of effluent to clays raised levels of nitrogen and calcium in the resulting complexes substantially, while phosphorus content increased significantly. Carbon content also increased substantially. Generally, levels of other elements hardly changed or else decreased relative to those in the clays, indicating that most or all of these elements are provided by the clays. The different washing and drying treatments (a-c) had no consistent effect on composition.

The net composition of the nutrient elements, N, Ca and P, in the complexes, as well as their protein contents, are expressed in Table 7 in relation to the major elements provided by various animal feeds and also fertilisers. Only values for complexes prepared by the simplest procedure (1, under section 4 of Research Methodology) are given.

The composition of hydrolysable nitrogen, indicating available amino acids, in the complexes was:

8,815 µg.g<sup>-1</sup>, ie. 0.88% in the complex formed with Saponite clay, and 4,200 µg.g<sup>-1</sup>, ie. 0.42% in the complex formed with Truben clay

Table 7. Nutrients available in clay-effluent complexes and in some animal feeds and fertilisers

Materials		С	omposition	ı (%)		Reference
	Protein	Ca	P	N	K	
Clay-effluent complexes (net composition )					•	
Saponite	3.72	0.36	0.13	1.46	0	
Truben	1.62	0.24	0.1	0.85	0	
JNB	1.48	0.22	0.08	0.86	0	
Animal feeds					-	
Alfalfa hay	15	1.5	0.2	2.5	2	Morrison,
Blood meal	80	0.4	0.3	13	0.1	Average (av.)
Bone, cooked	13 - 26	27	11.5	4	0	Range, av
Com	9	0.02	0.28	n.d.	0.30	Lassiter
Cow's milk	28	1	0.9	n.d	1.4	Leche
Hotel & restaurant garbage	4	0.1	0.1	0.7	n.d.	Morrison
Fertilisers Pertilisers						
Blood and Bone (Plant Life,	n.d.	15,12	5	5	2	
Yates)§						
Lawn Food (Grow Plus) <sup>§</sup>	n.d.	4	1.7	12.5	5	
Soluble (Thrive) <sup>§</sup>	n.d.	n.d.	5.5	27	9	
Duck, Goose & Turkey manure	n.d.	n.d.	0.3-0.7	1.1-1.3	0.4	Western
Farmyard manure	n.d.	n.d.	0.1	0.7	0.5	Russell

net composition = composition of complex - composition of clay

References denoted by first author's name.

Table 7 shows that the clay-effluent complexes provide lower levels of nutrients as animal feeds than most other materials shown apart from hotel and restaurant garbage. Nonetheless, the clay component of the complex (bentonite), while not providing nutrients directly, is acknowledged as a useful addition to animal feed in its own right. In animal feed, it acts as a growth promoter, largely by slowing passage of food through the digestive system and a toxin binder, decreasing losses by mortality and in performance from disease. In poultry, additions of 1% bentonite to feed led to weight gains of up to 32% and additions of 1.5% led to increases of up to 15% in egg production (Saeed, 1996, p. 47-51). As an additive in food for dairy cows, it raised milk yield by up to 10% and increased wool growth in sheep (Roskill, 1997). It control acidosis in rumen, caused by rapid fermentation of starches in grain feed (Carmichael, 1995).

As a fertiliser for plant growth, clay-effluent complexes would provide similar amounts of nitrogen and phosphorus as manures, but considerably less than either blood-and-bone or synthetic fertilisers of all nutrients (Table 2). However, the clay component could assist in increasing the water- and nutrient-holding capacities, especially of sandy soils.

n.d. not determined

s trade names

<sup>‡</sup>average, or range, of values given by Morrison, Lassiter and Leche

Table 8. Removal of toluene from solution in water by clay-effluent

Clay	Method of preparation of complex	% Toluene removal
Truben	1. Maximising protein uptake	75
	2. Maximising protein removal	54
Saponite	1. Maximising protein uptake	71
	2. Maximising protein removal	50

The associations of clay with were reasonably efficient at removing toluene, according to Table 8. However, excess effluent, rather than clay complex, may have attracted toluene, especially when associations were formed by maximising protein uptake. In these cases, only 62-72% of protein was removed from the effluent. There will be few situations where it is desirable to treat water with effluent, even within a complex with clay. The subsequent reduction of one type of contaminant (eg. hydrocarbons) would be offset by the addition of another, biologically active contaminant.

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#### **ANALYSIS OF FINDINGS AND OBSERVATIONS**

## Assessment of likely means of approach in abattoirs

#### Summary

The purpose of this study was to investigate the feasibility of the use of clays to remove proteins from abattoir wastewater, and to identify opportunities for the profitable application of the derived co-products.

The application of this adsorbent clay technology to meat industry waste streams primarily involves four steps. These steps are:

- 1. Addition and dispersal of clay;
- 2. Formation of the clay/protein complex (incubation);
- 3. Recovery of the clay/protein complex; and:

#### 4. Stabilisation of the filter cake.

Potential processing options, which might be successfully used to complete each of these process steps, are described separately below.

#### Adsorbent Clay Processing.

The presence of high concentrations of fat in abattoir wastewater would likely have a negative effect on the settling of the clay/protein complex. Therefore, this process is envisaged as operating subsequent to Dissolved Air Flotation (DAF) system where the fat content of wastewater has been minimised.

#### Step 1: Addition and Dispersal of clay.

The clay concentration required to achieve 100% protein removal was determined experimentally using wastewater samples from an operating abattoir. In a production situation, the required rate of clay addition is related to the wastewater flow rate and protein load. In order to ensure addition of the required amount of clay and complete dispersal (thus avoiding clumping of partially wetted clay) two options are proposed.

- 1. Clay be dispensed from a storage hopper into the wastewater immediately prior to a high shear, flow through mixer. The rate of addition of the clay can be controlled through a variable-speed drive on the dispenser.
- 2. A volume of wastewater is diverted into a mixing/dosing tank with the required weight of clay and mixed continuously to form concentrated clay slurry. This slurry is then dosed at the required rate, into the wastewater flow by a variable-speed dosing pump. Complete dispersal is then provided either by a short length of piping designed to generate turbulent flow, or a high shear, flow through mixer.

#### Step 2: Formation of the clay/protein complex.

The electrostatic adsorption of protein to clay is a function of the close proximity of clay layer charge to the clay surface. Once the clay has been completely dispersed in the wastewater, the interaction between clay and protein is extremely rapid. The necessary incubation time should easily be achieved in the pipes between the Dispersal and Recovery stations.

## Step 3: Recovery of the clay/protein complex.

Laboratory experiments have shown that settling of the clay protein complex can be effected in as little as 30 minutes. Two options for clay/protein complex recovery are proposed.

 Clay treated wastewater enters at the midpoint of an upright cylindrical settling tank, with a conical base. Wastewater enters the tank tangential to the cylinder body, setting up a slow circulation in the tank. The natural settling action of the clay/protein complex acts to concentrate the solids in the conical base, while the clarified wastewater overflows from the top of the tank. The concentrated solids

- are drawn from the base of the settling tank and dewatered using a belt or drum filter.
- 2. Clay treated wastewater is pumped at high velocity into a separation system consisting of hydrocyclones, which clarify the wastewater, and generate a concentrated clay/protein sludge. This sludge may require further de-watering (using a belt or drum filter) or may be directly suitable for stabilisation.

Step 4: Stabilisation of the filter cake. The de-watered sludge (filter cake) will likely contain sufficient moisture and nutrient to promote rapid microbial growth if stored at ambient temperatures. The two obvious options for stabilising this material are:

- 1. Returning the sludge to rendering for drying and addition to meatmeal. This recovered protein would increase the meatmeal yield while the presence of clay in animal diets has been shown to provide a benefit to animal health.
- 2. Addition of sludge to gut content etc. for composting and production of potting mix. Clay would improve the moisture-holding capacity of potting mixes and the clay-protein complex would act as a slow release nitrogen fertiliser.

## **Assessment of Economic Feasibility**

#### Introduction

In the previous section, two options for the stabilisation and utilisation of the clay/protein complex were suggested. A brief examination of the returns from adding the recovered protein to meat meal indicates this is unlikely to be feasible. The better option is to value add this material as a component of potting mix. For this to be possible, an abattoir would need to have a composting operation either on site or in the immediate vicinity.

#### Legislative Pressure.

Considerable pressure has been brought to bear on the operators of abattoirs by the release in 1995 of Draft Environmental Guidelines for the Utilisation of Treated Effluent by Irrigation by the New South Wales Environmental Protection Agency, and the subsequent amendment to the Pollution Control Bill (Load Based Licensing).

Compliance will require significant additional wastewater infrastructure eg. More land for irrigation, wet weather wastewater storage, and ongoing wastewater monitoring. In 1998, an estimate of the cost of compliance with the Irrigation Guidelines and Load Based Licensing (LBL) was prepared by Dr L. Atkinson of Australian Meat Technology, on behalf of the Country Meatworks Association of NSW. The cost of compliance for individual meat processors in NSW ranged between \$400,000 and \$5,500,000.

In simple terms, the costs associated with the Irrigation Guidelines and Load Based Licensing revolve around two types of load; the organic load (the mass of organic material in the wastewater) and more importantly the hydraulic load (the volume of wastewater for irrigation).

The technical solution to this problem is to recover the organic load and recycle the water thus minimising both organic and hydraulic irrigation loads. The economic challenge is to identify technologies that achieve load reduction in a cost-effective manner.

#### Selecting the Waste Streams for Treatment.

Treating the entire wastewater load from an abattoir with this clay technology would involve significant capital expenditure for minimal return. A far more useful option involves treatment of selected high COD (Chemical Oxygen Demand) waste streams, which are the major source of protein in wastewater. A technical report commissioned by the Meat Research Corporation (Environmental Issues Project M445: Identification of Nutrient Source Reduction Opportunities and Treatment Options for Australian Abattoirs and Rendering Plants) identifies four areas of abattoir operations that produce the bulk of wastewater contamination. These areas are (i) Slaughter and Evisceration, (ii) Offal processing, (iii) Manure and Paunch contents, and (iv) Rendering. Of these four areas, clearly the Rendering operations generate the greatest daily mass of COD.

#### Proposed Process outline

Clay is dispensed from a storage hopper by means of a variable speed screw conveyor. The rate of addition of the clay can thus be altered to suit the prevailing conditions. The clay drops into the incoming wastewater stream, and together the clay and wastewater drop into the dispersal tank, providing some initial mixing. Complete dispersal of the clay is achieved with a recirculating chopper pump. Once the wastewater in the tank reaches a predetermined level, a fraction of the pump flow is diverted so that the tank inflow and outflow are balanced and recirculation continues to ensure complete clay dispersal. A Vaughan chopper pump was chosen for its ability to recirculate and disperse the clay as well as supply sufficient outflow pressure to drive the subsequent clay/protein complex recovery. Recovery of the clay/protein complex is achieved using hydrocyclone technology.

#### Economic Feasibility

A spreadsheet financial model was constructed based on the addition of clay to wastewater from a continuous wet rendering plant at an abattoir slaughtering 900 head of cattle per day. The abattoir has an existing composting operation. The worksheets, which form the financial model, are presented in Appendix 1 through Appendix 4.

Clay is added at a rate that maximises protein uptake per gram of clay. At this concentration, the clay is expected to remove 58% of the total wastewater protein (Appendix 1). The installed cost of the clay/protein recovery plant is \$48,500 as outlined in the flowsheet in Appendix 2.

Addition of clay protein complex to other abattoir waste materials for composting will likely improve the water holding capacity and nitrogen content (slow release) of the final potting mix product. These attributes are assumed to attract a premium (\$5/tonne) over that charged for common potting mixes (\$30/tonne).

One of the key factors affecting the profitability of the proposed composting operation is how much clay/protein complex (dry weight basis) to add to the compost mixture (the level of inclusion of recovered clay/protein). Inclusion levels from 10 to 40% were tested in the financial model to gauge the effect on the Payback Period for the process. Inclusion levels above 35% resulted in payback periods greater than seven years. The ideal inclusion level is assumed to be in the range between 20 and 30% of total dry mass (payback in 1.6 to 3.75 years).

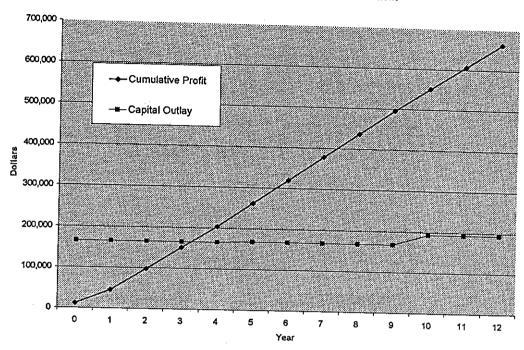
Subsequently, the financial model assumed the clay/protein complex to account for 30% of the dry matter in the final product. A lower clay/protein content will improve the profitability of the product so long as the selling price is maintained.

The potting mix is assumed to be a bulk product with no packaging. Significantly higher returns may be achieved in the (small volume packaged) retail market however additional cost would also be incurred through packaging and distribution of the product.

Assuming an inclusion level of 30% and a selling price of \$35 per tonne the projected Cash Flow (Appendix 3), and Profit and Loss (Appendix 4) statements for the proposed composting operation were generated for a twelve-year period. These projected figures were used to chart the Payback Period and the Internal Rate of Return (IRR) for this process. The Payback and IRR charts are shown in Figures 1 and 2 respectively.

Figure 8: Payback Period

## Payback Period for Total Investment



The Payback Period indicated by the crossover of the graphs for Cumulative Profit and Capital Outlay in Fig. 8 is approximately 3.75 years of operation.

Figure 9: Internal Rate of Return

#### Internal Rate of Return

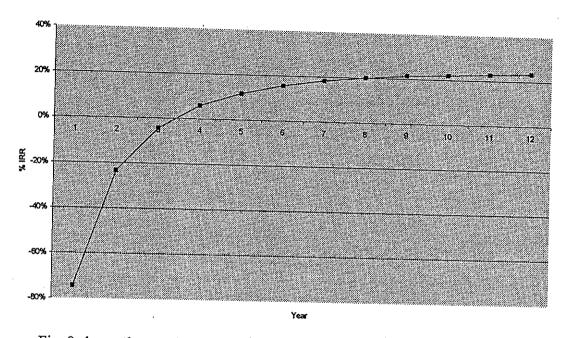


Fig. 9 shows the graph of IRR approaching a maximum value of approximately 22%.

## **CONCLUSIONS DRAWN**

It is possible, using clay, to remove all protein from wastewater. Under normal economic circumstances however, complete protein removal is not the most cost-effective use of this technology. A far more cost-effective application of this technology involves the recovery of a significant proportion of the organic load from abattoir wastewater and the use of those proteins to value add an existing composted product.

Secondary benefits may also be gained indirectly through the reduction of organic load on current waste treatment and disposal options. However, the economic benefits associated with the reduction of waste organic load must be determined for each individual abattoir as these benefits will vary according to the specific waste management situation. For example, the organic material in wastewater in some abattoirs is decomposed by mechanical aeration in ponds. In these cases, a decrease in the protein load through the use of clay will lead to a reduction in the consumption of electricity used for mechanical aeration.

If the financial benefits of waste load reduction are ignored, and the composting operation is considered in isolation, then the financial model indicates that composting of clay protein enriched abattoir waste remains profitable if the product can be sold at a minimum of \$35 per tonne.

The two factors, which have the greatest negative impact on the economics of this process, are the relatively high cost of clay and the protein binding capacity of clay. These two negative factors could be addressed (and thus the economics of protein recovery using this technology would be improved) through:

- 1. Increasing the capacity of clay to bind protein (perhaps through pre-treatment)
- 2. Devising a method for recycling the clay for repeated use.

#### RECOMMENDATIONS

It is recommended:

- 1. The removal of proteins from selected wastewater streams in abattoir operations be trialled at a pilot scale, and
- 2. The performance of the products of treatment of these wastewaters with clays as slow-release fertilisers be tested by plant growth trials.

## CONSEQUENCES OF THE RECOMMENDATIONS

Following a successful trial at pilot scale, application of clay to abattoir wastewater, especially as produced from rendering operations would:

- reduce the organic load in wastewater for disposal
- produce a product with resale value

#### IMPLEMENTATION PLAN

- 1. Establish a pilot plant for the treatment of selected wastewater by clay as part of the operations of an abattoir.
- 2. Test the use of the product from the pilot plant as a fertiliser in agronomic trials.

## **Acknowledgments**

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## Appendix 1: Flowsheet for Recovery of Wastewater Protein using Clay

Financial Assumptions	
Borrowings	60000
Period of Loan (Number of years)	25
Interest Rate (Interest only loan)	7.25%
Interest Rate on Invested Funds	5.00%
CPI (2%) Tax rate	1.02
Depreciation Rate - Plant & Equipment (%)	36%
	20.00%
Capacity and Operation of Manufacturing Plant	
Estimated selling price (potting mix (\$/tonne))	\$35.00
Estimated annual production (tonnes of potting mix) Clay/protein content of potting mix	9957
Production capacity year 0	30% 50%
Production capacity year 1	75%
Production capacity year 2-12	100%
Protein Recovery	70070
Wastewater flow rate (L/min)	. 60
Operating hours per day	14
Operating days per year	250
Daily wastewater treatment volume (L) Wastewater Total Solids	50400
Wastewater Protein	6.5%
Wastewater protein content (g/L)	4.35% 43.5
Daily wastewater protein loss to ponds (kg dry mass)	2192.40
Projected protein recovery	58%
Clay:protein ratio	1.60
Clay addition rate (g/L)	69.6
Daily clay requirement (tonne)	3.51
Cost of clay (\$/tonne)	\$150
Daily cost of clay Daily cost of electricity	\$526.18
Daily clay/protein production (kg dry mass)	\$49.00 4779
Labour requirement- protein recovery (hours per day)	4779
Hourly rate (\$/hour)	17
Labour On-costs	20%
Daily cost of labour (protein recovery)	\$40
Composting	
Daily requirement for compostable material	11152.01
Daily cattle kill	900.00
Mean weight of paunch content (kg) Total Solids in paunch content	38.30
Dry weight of paunch solids (kg)	7.20%
Wet weight of paunch solids (kg)	2.76 27.58
Daily available paunch content (kg dry wt)	2481.84
Daily requirement for manure/bulking agent (kg dry wt)	8670.17
Cost of Manure/bulking agent (\$/tonne dry wt)	25
Labour requirement- composting (hours per day)	10
Daily cost of labour (composting)	200
Moisture content of final product	60%
Daily production of potting mix (tonnes)	40
Equipment	
Clay hopper and feed screw	\$8,000
Dispersal tank	\$5,000
Recirculating chopper pump	\$18,000
Hydrocyclones Installation	\$2,500 \$15,000
,	\$15,000
Total	\$48,500

Appendix 2: Capital Requirements

Particulars	Year 0	Year 1	Year 2	Year 3 Year 4	Year 4	Year 5	Year 6	Year 7	Year 8	Year 9	Year 10	Year 8 Year 9 Year 10 Year 11	Year 12
Step. 1 - Addition & Dispersal Clay hopper and feed screw Dispersal tank Recirculating chopper pump	8,000 5,000 18,000										21,942		· .
Step 2 - Clay/Protein Recovery Hydrocyclones	2,500					2,760					3,047		
Installation	15,000									•			
Total New Capital Cumulative New Capital	48,500 48,500	0 48,500	0 48,500	0 48,500	0 48,500	2,760 51,260	0 51,260	0 51,260	0 0 0 51,260 51,260 51,260	0 51,260	24,989 76,250	76,250	0 76,250

Appendix 3: Cashflow

Particulars Inflows Revenue	Year 0	Year 1	Year 2	Year 3	Year 4	Year 5	Year 6	Year 7	Year 8	Year 9	Year 10 10	Year 11 11	Year 12 12	•
Borrowed Funds % of capacity Sales Interest Received	60,000 50% 174,250	75% 261,375 600	100% 348,500 2,280	100% 348,500 2,364	100% 348,500 2,368	100% 348,500 2.368	100% 348,500 2.368							
Total Revenue	234,250	261,975	350,780	350,864	350,868	350,869	350,869	350,869	350,869	350,869	350,869	350,869	350,869	
Total Inflows	234,250	261,975	350,780	350,864	350,868	350,869	350,869	350,869	350,869	350,869	350,869	350,869	350,869	
<b>Qutflows</b> <u>Capitalisation</u> Refer Capital worksheet	48,500	0	0	0	0	2,760	٥	0	0	0	24,989			
Total Capital Expenditure	48,500	0	0	. •	0	2,760	0	0	0	0	24,989	• •	• 0	
Eixed Expenses Interest Repay on Borrowings Capital Repay on Borrowings	4,350 25,000	35,000	00	0	0	0	0	0	0	0	0	0	0	
Total Fixed Expenses	29,350	35,000	0	0	0	0	0	0	Ó	0	0	0	0	
Operating Expenses Bank Charges & Fees Blectricity Clay Manure/Bulking agent Labour cost (protein recovery) Labour cost (composting)	1,000 12,250 65,772 27,094 9990 24975	1,000 12,250 98,658 40,641 9990 37462.5	1,000 12,250 131,544 54,189 9990 49950											
Total Operating Expenses	141,081	200,002	258,923	258,923	258,923	258,923	258,923	258,923	258,923	258,923	258,923	258,923	258,923	
Taxation	6,883	18,714	29,602	29,639	29,641	32,854	32,887	32,888	32,888	32,888	30,976	31,294	31,310	
Total Outflows	225,814	253,716	288,525	288,562	288,564	294,537	291,809	291,811	291,811	291,811	314,888	290,216	290,232	
Annual Net Cashflow	8,436	8,259	62,256	62,302	62,305	56,332	59,059	59,058	59,058	59,058	35,980	60,652	60,637	

Appendix 4: Profit and Loss

Profit and Loss

Particulars Inflows Bevenue	Year 0	Year 1	Year 2	Year 3	Year 4	Year 5 5	Year 6	Year 7	Year 8	Year 9	Year 10 10	Year 11	Year 12
% of capacity Sales (FSH ConA) Interest Received	50% 174,250	75% 261,375 310	100% 348,500 2,350	100% 348,500 2,454	100% 348,500 2,459	100% 348,500 2,235	100% 348,500 2,326	100% 348,500 2.331	100% 348,500 2.331	100% 348,500	100% 348,500	100%	100% 348,500
Total Revenue	174,250	261,685	350,850	350,954	350,959	350,736	350,827	350,831	350,831	350,831	349.966	350.848	2,391
Total Inflows	174,250	261,685	350,850	350,954	350,959	350,736	350,827	350,831	350,831	350,831	349.966	350.848	350.892
Outflows Eixed Expenses Depredation													
- Plant & Equipment Interest Repay on Borrowings	9700 4,350	0. 0 0	9700	9700	9700	552 0	552 0	552 0	552 0	552	4998 0	4998	4998
Total Fixed Expenses	14,050	9,700	6,700	9,700	9,700	552	552	552	552	552	4.998	4.998	2 998
Operating Expenses Bank Charges & Fees Electricity	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1.000	1 000	6	5
Clay Manura/Bulking agent	65,772	98,658	12,250 131,544	12,250 131,544	12,250 131,544	12,250 131,544	12,250 131,544	12,250	12,250	12,250	12,250	12,250	12,250
Labour cost (protein recovery) Labour cost (composting)	27,094 9,990 24975	40,641 9,990 37462.5	54,189 9,990 49950	54,189 9,990									
Total Operating Expenses	141,081	200,002	258,923	258,923	258,923	258,923	258,923	258,923	258,923	258,923	258,923	258.923	258.923
Total Outflows	155,131	209,702	268,623	268,623	268,623	259,475	259,475	259,475	259,475	259,475	263,920	263,920	263.920
Net Profit/Loss before Tax Previous Years Losses	19,119	51,983	82,228	82,332	82,337	91,261	91,352	91,357	91,357	91,357	86,046	86,928	86,971
Total Taxable Income	19,119	51,983	82,228	82,332	82,337	0 91,261	0 91,352	0 91,357	0 91,357	0 91,357	0 86,046	0 86,928	0 86,971
Taxation	6,883	18,714	29,602	29,639	29,641	32,854	32,887	32,888	32,888	32,888	30,976	31,294	31,310
Net Profit/Loss after Tax	12,236	33,269	52,626	52,692	52,696	58,407	58,465	58,468	58,468	58,468	55,069	55,634	55,661
Cumulative Profit after Tax	12,236	45,505	98,131	150,823	203,519	261,926	320,391	378,859	437,328	495,796	550,865		662,161