

Properties and cleanability of new and traditional agricultural surface materials

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The aim of the present study was to evaluate new and traditional surface materials for use in cattle barns. The evaluated concrete materials had different compositions and included different additives and coatings. Contact angle meter, optical profilometry and scanning electron microscopy SEM were used for characterization of surface properties. Radiochemical methods and a biochemical adenosine triphosphate ATP method were used to determine cleanability. A specific methodological aim was to examine the correlations between these determination methods. A statistically significant difference was observed between contact angles of non-coated concretes, coated concretes and joint materials. In general, coatings smoothed surfaces and the joint materials were the roughest surfaces, as illustrated by profilometry and SEM. On the basis of the radiochemical determination methods, coatings improved the cleanability of concrete. An epoxy joint material was cleaned efficiently from the oil model soil and from the labelled feed soil when compared to the two cement-based joint materials. According to the results of the biochemical ATP method the manure test soil was cleaned better from a concrete including inorganic sealant than from the other materials examined. The cleanability results of oil model soil used in the radiochemical method correlated with the results of the test feed soil used in the biochemical ATP method. Both determination methods of cleanability appeared to be suitable for examining the cleanability of surfaces soiled with agricultural soils. Only the radiochemical determination gives detailed quantitative results, but it can be used only in laboratory studies. The results of this laboratory study will be used for selecting materials for a pilot study in a cattle barn.

Key-words: Cleanability, animal house, flooring, radiochemistry, gamma spectrometry, liquid scintillation counting, ATP, bioluminescence, SEM, contact angle

Introduction

Material choices in agricultural environments affect animal welfare, hygienic condition of surfaces and products, and the working environment of the personnel. Many demands are applied to floorings in animal buildings. The flooring should withstand strong mechanical and chemical stresses, and when used in lying areas for animals it should also be comfortable to lie on. The flooring should not cause injuries, diseases, distress and discomfort or inconvenience to animals (Baxter 1984). The properties of the flooring materials which must be considered include e.g thermal comfort, softness, friction, abrasiveness and contact pressure between animal and floor (Nilsson 2005). The cleanability of surfaces is one aspect affecting the choice of flooring material for cattle barns. In general, a smooth flooring can be kept clean more easily than a rough flooring (Hörndahl 1995). However, when evaluating surface materials used in animal houses it should be remembered that surfaces which are too smooth may be slippery for animals and personnel, and cause injuries. The amount of soil and moisture on the flooring influence the floor properties; above all soil affects the slipperiness (Nilsson 2005).

Concrete is a very generally used floor material in agricultural buildings. Although concrete is a material which is often well suited for agricultural environment, it is far from being unaffected by many environmental hazards (Nilsson 2005). Animals and vehicles wear floorings mechanically, and feeds, milk and manure represent chemical hazards for concrete (Table 1).

According to De Belie et al. (2000) the durability of concrete against attack by lactic and acetic acids has been improved in many ways, e.g. by using different cement types and pozzolanic additives, changing the aggregate type, addition of polymers to the concrete mix, application of cement-bound surface layers and impregnation with water repellents or pore blockers or application of coatings. Coatings can be used to limit water penetration into concrete, which is a porous material. Substances soaked into reinforced concrete materials are the main reason for its disintegration (Barbucci et al. 1997).

In previous studies concerning the cleanability of animal houses, different evaluation methods such as visual (Sundahl 1974, Puumala and Lehtiniemi 1993, Hörndahl 1995, Larsson 2000, Zhang et al. 2006), microbiological and biochemical (Larsson 2000, Pelletier et al. 2002, Small et al. 2007) and optical methods (Zhang et al. 2006) were used. In the study by Kymäläinen et al. (2008), radiochemical and colorimetric methods were used for comparing the cleanability of concrete and plastic coatings for use in piggeries. Radiochemical methods have earlier been used for flooring materials in public buildings (Ohlson and Wäänänen 1971, Jokelainen and Uusi-Rauva 1976, Engström and Bäckström 1987, Pesonen-Leinonen et al. 2006, Määttä et al. 2007a). These methods provide quantitative information on the amount of soil both on the surface and soaked into the material. This capability is especially important when porous materials such as concrete are evaluated. The biochemical ATP method provides information on the biological contamination on surface. The ATP method has been used to determine

Table 1. Chemical substances and contaminants of concrete in cattle barns.

Source	Acid	Effect	Reference
Silage	Lactic, acetic, butyric	Acids weaken slowly	ACI 515.1R-79 1985, Bertron et al. 2005, Nilsson 2005
Milk	Lactic	Fresh milk harmless, fermented lactic acid weakens slowly	ACI 515.1R-79 1985
Manure	Acetic, propionic, butyric, iso-butyric	Acids weaken slowly	ACI 515.1R-79 1985, De Belie et al. 1996, Bertron et al. 2005
Urea	-	Harmless for concrete	ACI 515.1R-79 1985

- not included

the cleanability of surfaces from organic soils in the food industry and in public and hospital buildings (Poulis et al. 1993, Kuisma et al. 2003, Larson et al. 2003, Pesonen-Leinonen et al. 2003, Aycicek et al. 2006, Redsvén et al. 2007).

The aim of the present study was to examine the surface properties and cleanability of new and traditional surface materials. The effects of different compositions and additives and coatings on the cleanability of concrete flooring were examined. The materials prepared and evaluated were intended for use in floorings and feeding tables in cattle barns. In addition, the cleanabilities of joint materials to be used with ceramic tiles e.g. in milk rooms were evaluated. Results from the laboratory studies will be used when selecting materials for a pilot study in a cattle barn.

Materials and methods

Radiochemical methods with three labelled model soils and two labelled natural soils were used for

evaluating cleanability. In addition, a biochemical ATP method was used for assessing cleanability of the surfaces from organic soils. The surface properties were examined by determining water contact angles and surface roughness parameters.

Laboratory-made and commercial surface materials

The materials evaluated are presented in Tables 2 and 3. Epoxy, polyurethane, acrylic and polyester were used as surface coatings. The thicknesses of the coatings varied between 0.5 mm and 5 mm. The basic cement paste was in some cases treated with fluosilicate or an inorganic sealant. Fluosilicate was brushed and soaked to the sandblasted sample surface, whereas inorganic sealant was brushed and sprayed on (Table 3). In addition, the cement paste without any coating or extra treatment was examined. In all experimental materials, the basic cement paste was laboratory-made, whereas commercial versions of the other materials were examined. However, not all the materials are used

Table 2. Codes and compositions of the evaluated surface materials and their possible use in cattle barns.

Code	Components		Experimental material (E) or material already in use (U)	Site		
	Substrate	Surface coating or treatment		Floor	Feeding table	Joint
J1	Joint material, cement-based	None	E	-	-	X
J2	Joint material with additives, cement-based	Fluorochemical	E	-	-	X
J3	Joint material, containing epoxy	None	U	-	-	X
C1	Cement paste	Trowelled	U	X	X	-
C2	Cement paste	Fluosilicate	U	X	X	-
C3	Cement paste	Inorganic sealant	E	X	X	-
Co1	Fibre cement	Acrylic coating	U	X	X	-
Co2	Fibre cement	Polyurethane coating	U	X	X	-
Co3	Cement paste	Epoxy coating	U	X	X	-
Co4	Concrete	Polyester coating	U	-	X	-

-not suitable

Table 3. Manufacturing and formulation of substrates and surface coatings or treatments.

Code	Manufacturing of components			Surface coating or treatment	
	Substrate	Type	Manufacturing	Type	Manufacturing
J1	Joint material, cement-based		Dry mix : water = 10 kg : 3 kg	None	-
J2	Joint material with additives, cement-based		Dry mix : water : copolymer = 10 kg : 1.7 kg : 0.4 kg	Treatment with fluorochemical by spraying liquid	Joint protector 0.014-0.03 kg/m ²
J3	Joint material, containing epoxy (DeLaval)		Epoxyresin mix : additives : sand = 0.88 kg : 0.22 kg : 1.9 kg	None	-
C1	Cement paste		Cement : stone/sand : water : additives = 14 kg : 79 kg : 8 kg : 0.05 kg	Trowelled	-
C2	Cement paste		As in C1	Treatments twice with fluosilicate by brushing and sinking (for 24h)	First cycle: liquid : water = 9 kg : 65 kg Second cycle: liquid : water = 16 kg : 65 kg
C3	Cement paste		As in C1	Inorganic sealant applied by brushing and spraying	Brushing : dry product : water = 5 kg : 2 kg, Spraying: liquid product : water = 1 kg : 3 kg
Co1	Fibre cement* (Minerite)		Cement, cellulose fibre and mineral fillers	Acrylic coating (5 mm) (Nanten)	Sand addition (7 kg/m ² , granule size 0.6 – 1.2 mm)
Co2	Fibre cement* (Minerite)		Cement, cellulose fibre and mineral fillers	Polyurethane coating (3 mm) (Nanten)	Sand addition (0.4 – 0.7 volume % of amount of polyurethane, granule size max 1 mm)
Co3	Cement paste		As in C1	Epoxy coating (2 mm) (DeLaval)	Sand addition (3 kg m ² , granule size 0.9 mm)
Co4	Plastic concrete		Polyester resin : stone/sand : fillers : aggregates	Same as substrate (0.5 mm)	Surface (coating) made by heating the surface of substrate

- no surface coating

*For production technical reasons, fibre cement substituted a paste/concrete surface in this study. The surface coating was relatively thick in this study, and was considered to be unaffected by the substrate.

in animal houses or marketed for that use at present. Three different joint materials were also evaluated (Table 2). Two of them were cement-based clinker joint materials, one of which was treated by spraying with fluorochemical (Table 3). The third joint material was a commercial clinker joint material containing epoxy.

Cleanability experiments and characterization of surfaces

The experimental design of determination of cleanability and surface properties is presented in Fig. 1. Two different radiochemical determination methods, a gamma-spectrometric method and liquid scintillation counting, were used for evaluation of the cleanliness of the surfaces (Fig. 1). The radioactivity of a surface is comparable to the amount of labelled isotope on the surface. ATP bioluminescence is a rapid method for monitoring the cleanliness of surfaces (Fig. 1). The method is based on the hydrolysis of ATP by luciferase enzyme, detected by a luminometer and reported as

relative light units (RLU). Surface properties were examined using a contact angle meter, an optical profilometer and a SEM.

Soils

Three model soils and two labelled natural soils were used in the radiochemical study (Table 4) and manure and feed soils were used in the biochemical ATP study. In order to obtain natural soils suitable for the cleanability experiments, manure and feed were mixed with purified water and other substances (Table 4). The amounts of the radiochemical model soils were the same as used in our earlier studies (Määttä et al. 2007a). The amounts of the natural soils were selected in order to assist dosage and according to the detection limit of the ATP method.

In the ATP study the manure the manure soil (soil 6) consisted of 30 g manure and 48 ml water. The soil was collected from a cattle barn (Minkiö, Finland) in the summer of 2005 as a batch of 10 kg, homogenised and divided into 10 g packages in small plastic bags and stored in a freezer. The

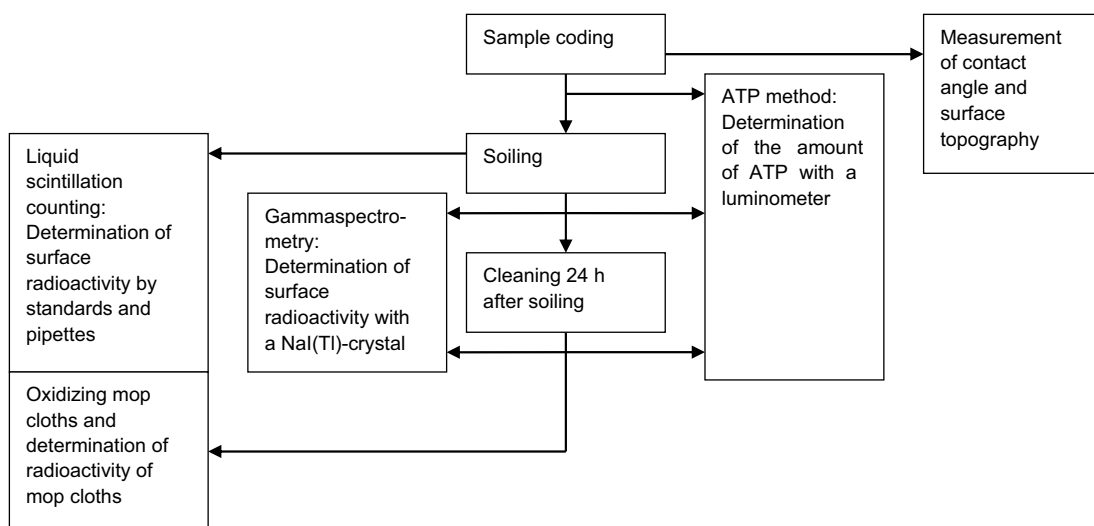


Fig. 1. Experimental design of the determination of cleanability and surface properties.

Table 4. Compositions and amounts of soils used in the radiochemical study. In radiochemical model soils, triolein refers to glyceryl trioleate.

Type of the soil		Components and their relative amounts (g or ml) of the soil mixtures				Amount of soil (µl) on a disc
		Chromium component	Solvent	Other components or substances	Radio-isotope	
1	Inorganic particle model soil	Chromium (III) oxide (Cr ₂ O ₃) (m=0.40 g)	1-propanol (V=10 ml)	Triolein (C ₅₇ H ₁₀₄ O ₆) (0.60 ml)	⁵¹ Cr	50
2	Organic particle model soil	Chromium acetyl acetate (C ₁₅ H ₂₁ CrO ₆) (m=0.40 g)	1-propanol (V=10 ml)	Triolein (C ₅₇ H ₁₀₄ O ₆) (0.60 ml)	⁵¹ Cr	50
3	Organic oil model soil	Chromium (III) oxide (Cr ₂ O ₃) (m=0.40 g)	1-propanol (V=10 ml)	Triolein (C ₅₇ H ₁₀₄ O ₆) (0.60 ml)	¹⁴ C	50
4	Labelled manure soil	Chromium (III) oxide (Cr ₂ O ₃) (m=0.15 g)	Water (V=16 ml)	Manure (m=10 g)	⁵¹ Cr	625
5	Labelled feed soil	Chromium (III) oxide (Cr ₂ O ₃) (m=0.15 g)	Water (V=16 ml)	Feed (m=5 g)	⁵¹ Cr	625

composition of the manure soil was measured at Novalab Oy (Finland) using a gravimetric method for raw food fat and a Kjeldahl method for protein, and the amounts of carbohydrates, dry matter and ash were calculated. Manure consisted of dry matter (16.5%), combustible/matter ash (2.8%), raw food fat (1.5%), protein (2.9%) and carbohydrates (9.3%).

In the ATP study the feed soil (soil 7) consisted of 15 g feed and 48 ml water. The soil was a dry milk-based feed product, produced by Raisio Feed Ltd and intended for feeding of calves. According to information provided by the manufacturer, the composition of the feed was: moisture (12.5%), raw food fat (4.7%), crude protein (18.3%), raw fibre (5.3%), combustible remains (8.2%), calcium (1.1%), phosphorus (0.7%), magnesium (0.4%) and sodium (0.4%). The feed was stored at room temperature in a paper sack.

Inorganic particle and oil model soils were labelled both with the gamma-ray emitter ⁵¹Cr and the beta-ray emitter ¹⁴C and organic particle model soil was labelled with ⁵¹Cr. Natural manure and feed soils were also labelled with ⁵¹Cr when used as ra-

diochemical soils. The cleanabilities of different components of model soils can be determined by measuring the different radio-isotopes. In this study the ⁵¹Cr isotope labelled particle components and the ¹⁴C isotopes labelled the oil component.

Soiling and cleaning for the radiochemical method

Soiling with the radiochemical model soils was carried out with the procedure described earlier by Pesonen-Leinonen et al. (2006) and Määttä et al. (2007a) (Fig. 1). The samples were subjected to one soiling and cleaning cycle. The fluid model soils (50 µl) were applied to the middle of the sample (size 3 cm × 3 cm) with a pipette and 1-propanol was used as a carrier to assist dosage (Table 4). The natural soils (625 µl) were applied to the sample with a measure and deionised water was used to assist the dosage. The soils were left to dry for 24 ± 2 h at room temperature. Cleaning was carried out with a Mini Cleanability Tester (Pesonen-Leinonen

et al. 2006, Määttä et al. 2007a,b). The estimated pressure applied to the sample was 25 kPa, velocity 30 rpm and the number of revolutions was three. The cleaning head was equipped with a microfibre cloth (Freudenberg Household Products Oy Ab) (Pesonen-Leinonen et al. 2003, 2006, Määttä et al. 2007a,b). The material of the microfibre cloth was polyester (100%) and the pile length was 8 mm. The microfibre material is not used for cleaning cattle barns but was a part of the radiochemical method. For cleaning model soils the cloth was moistened at 100% weight regain compared to the weight of the dry cloth, with a 5% weakly alkaline detergent solution (Kuisma et al. 2005, Pesonen-Leinonen et al. 2006) and to clean natural soils the moisture regain was 200 %.

Measurement of cleanability using the radiochemical method

The radioactivity of the surface was a measure of the amount of the labelled component of soil on the sample. In this study we measured the removal of soil by measuring soil residues. Soil residue indicates how much soil remains on the surface after cleaning. The cleaning result was presented as the proportion of the labelled component of soil after cleaning compared to that after soiling. Five replicate tests were performed for each test combination.

The cleanabilities of the natural soils and model soils labelled with the gamma-ray emitter ^{51}Cr (Table 4) were determined by a gamma-spectrometric method using an NaI(Tl)-scintillation crystal (Fig. 1). The counting system is composed of a $2'' \times 2''$ NaI(Tl)-crystal detector (Bicron Corporation, Ohio, USA), coupled to a multichannel analyser and standard electronics (Canberra Inc., Connecticut, USA). The number of counts was recorded from 1 min to 5 min depending on the activity of the sample. The results were reported as counts per minute (cpm). The radioactivities of the soiled samples were measured before and after cleaning. The results were calculated by subtracting the activity of the background and correcting the results for radioactive decay.

The cleanability of model soil labelled with the beta-ray emitter ^{14}C (Table 4) was measured using liquid scintillation counting (Fig. 1). When preparing samples for measurement after cleaning, the concrete materials were too hard to be cut into pieces small enough without loosening activity, as reported in our earlier study on ceramic tiles (Määttä et al. 2007b). Therefore the activities of the mop cloths were measured in this case and the activities of the surface materials were calculated using these results. The mop cloths were oxidized in an oxidizer (Maricont 781, Junitek, Finland), radiolabelled carbon dioxide was trapped in a trapping agent and the radioactivity was measured with a liquid scintillation counter (Wallac 1411 Liquid Scintillation Counter, Wallac, Finland) and a measuring program (1414 WinSpectral™). The measurement time was 10 min. The results were reported as disintegrations per minute (dpm). The radioactivities of materials after soiling were determined using five dosages of soil. Calculation of the results included the attenuation equalizer and subtraction of the background. Correction for radioactive decay was not needed because of the long half-life of carbon.

Soiling and cleaning for the biochemical ATP method

In order to prepare experimental soils suitable for spreading on the surface material samples, the basic manure and feed soils were mixed with purified MilliQ water. The soils were prepared by pouring the soil and pipetting the water into a plastic bag (Stomacher Lab Systems Model 400 Bags, Seward Limited, UK) The mixture was allowed to stabilize for 30 min and homogenized in a Stomacher Circulator 400 (Seward Limited, UK) at 230 rpm for 5 min. Part (0.5 g) of the soil mixture thus obtained was applied to the sample (on an area of approximately 10 cm² in the middle of the surface sample) with a measure. The soils were left to dry for 24 ± 2 h at room temperature (Fig. 1).

Cleaning was carried out with the Erichsen Washability and Scrubbing Resistance Tester, model 494 (Erichsen GMBH and Co, Germany)

using the same microfibre mop cloth as in the radiochemical experiments. The cloth was moistened to 100% moisture regain with MilliQ water (no detergent was used). The surroundings of the sample to be tested were covered with plastic film to prevent cross contamination of the Erichsen machine and its parts. The surface samples were cleaned by moving the cleaning cloth back and forth across the sample. Five washing cycles were selected to represent approximately equal possible real cleaning practices. The estimated pressure applied to the sample was 1.4 kPa. Five replicate tests were performed for both soils.

Measurement of cleanability using the biochemical ATP method

ATP samples from the soiled surfaces were taken with sterile cotton swabs from an area of approximately 10 cm². The procedure was carried out according to the manufacturer's instructions. The ATP bioluminescence was measured luminometrically with the HY-LiTE[®]2 equipment (Merck KgaA, Germany). The intensity of light thus generated was read as relative light units (RLU). RLU is directly related to the amount of ATP and thus to the organic contamination on the surface. The samples were evaluated three times: before and after soiling and after cleaning (Fig. 1). The ATP amount of the samples before soiling was evaluated from five separate samples, the mean of which was used as a basic value for both soil cases.

Contact angle measurements

Repellence properties of the materials were evaluated by measuring contact angles using a CAM 100 contact angle meter (KSV Instruments Ltd, Finland). The contact angle of water was used to assess the hydrophobicity or hydrophilicity of materials. Static water contact angles on the experimental surfaces before soiling were measured. A water drop (MilliQ water) was placed on the surface and imaged for 40

seconds, collecting one image per second (Määttä et al. 2007a). The contact angles were presented as the mean of the last twenty images. Calculation of contact angle was based on the Young-Laplace equation. The result was the mean of the drop of five replicate samples. The sessile drop technique has earlier been used for concrete materials by Benzarti et al. (2006).

Topography assessment

Surface features and roughness parameters of the material surfaces were imaged and measured by means of an optical profiler provided with 2D and 3D imaging capabilities (Sensofar Plμ 2300). The material surfaces were imaged with 20× and 50× magnification. The measuring area was 0.64 × 0.48 mm² in the magnification 20× and 0.25 × 0.19 mm² in the magnification 50×. One image at each magnification was recorded and from each image five line profiles were measured. The R_a roughness values (the arithmetical mean deviation of the profile) were derived from the line profiles. In addition, images of the surfaces were taken using a SEM (JEOL JSM-840, USA) at 100×, 500× and 1500× magnifications. The magnification 500× illustrated the surface best and was used for each material.

Statistical methods

Statistical analyses were performed using SPSS version 12.0 (SPSS Inc., Chicago IL, USA), based on the mean values of the results. The cleanability results for each of the soils were analysed separately. The cleaning result in the radiochemical method was presented as the proportion of the soil residue after cleaning compared to the amount of soil on the surface after soiling. The cleaning results of the biochemical ATP method were presented as RLU-values before and after soiling and after cleaning. Analysis of variance was used to examine differences between the materials and treatments. Bivariate cor-

relation analysis (Pearson's correlation coefficients, two-tailed test of significance) was used to examine possible correlations between roughness values, contact angles and soil residues. The significance used was 0.05 in analysis of variance and 0.01 in analysis of correlation.

Results

Cleanability of the materials

The soil residues of radiochemical model soils of all the samples are presented in Fig. 2. The soil residues of the radiochemically labelled manure and feed soils (soils 4 and 5, respectively) were at the same level in the case of non-coated concretes and joint materials. On the plastic coatings the residues of labelled feed soil were lower than those of labelled manure. In accordance with this result, the coatings improved the cleanability of surfaces from labelled feed soil ($p = 0.021$ in the analysis of variance) but not from labelled manure soil ($p = 0.412$). In the case of simple model soils the soil residues of inorganic model soil 1 (chromium oxide and triolein labelled with ^{51}Cr) were the lowest (except for J3) and in general the soil residues of organic oil model soil 3 (chromium oxide and triolein labelled with ^{14}C) were the highest. According to soil residues, the coating improved the cleanability of concrete surfaces from

oil model soil (Fig. 2) ($p = 0.001$). In general the soil residues of the organic model soil (soil 2, chromium acetyl acetate and triolein labelled with ^{51}Cr) were at the same level as the soil residues of both labelled natural soils, but no statistically significant correlations were observed.

According to the cleanability results of the radiochemical study, polyester (Co4), acrylic (Co1) and polyurethane (Co2) coatings improved cleanability the most efficiently, whereas the cleanabilities of the non-coated concretes were the lowest (Table 5). Interestingly, the cleanability of non-coated concrete including inorganic sealant (C3) from manure soil (labelled ^{51}Cr) was better than that of coated concretes. According to the results in Table 5 the epoxy-coated concrete (Co3) was cleaned most efficiently from the labelled natural soils in the radiochemical study.

The cleanability of epoxy-based joint differed from that of the cement-based joint materials. The epoxy joint was cleaned more efficiently from radiochemical oil model soil than the other joint materials, whereas the two cement joints were better cleaned from the other radiochemical model soils (Fig. 2).

The ATP content of the manure soil was clearly greater on surfaces after soiling than that of the feed soil. Most of the surfaces soiled with the manure soil had a mean ATP content between 2500 RLU and 7000 RLU, whereas the mean ATP content of the surfaces soiled with the feed soil was below 200 RLU. As an exception, the surface C3

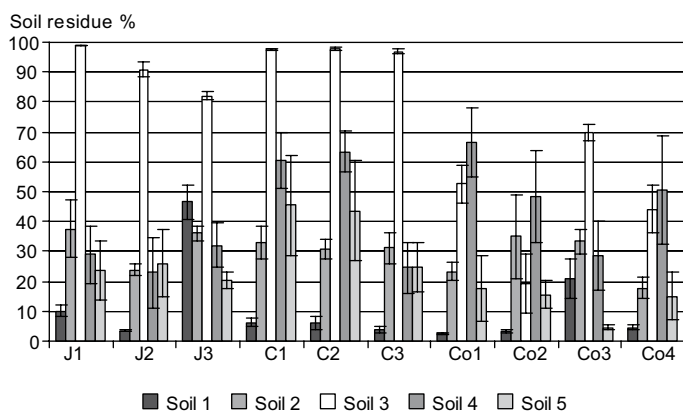


Fig. 2. Cleanability of the surfaces from five different soils as estimated by radiochemical measurements. The results are expressed as means (columns) and standard errors of means ($\pm\text{SE}$, bar) of five replicates. The lower the soil residue, the better is the cleanability result. The codes of the samples are presented in Table 2 and the codes of the soils in Table 4.

Table 5. Cleanability of the surface materials listed in order of superiority according to the radiochemical study and both the radiochemical and ATP method (the smaller number, the better the cleanability). Sum = results of all radiochemical soils (A) or all methods (B) added together. Radiochemical soils are presented in Table 4 and material codes in Table 2.

Code	Radiochemical method					ATP method			Both methods together		
	Soil 1 (⁵¹ Cr)	Soil 2 (⁵¹ Cr)	Soil 3 (¹⁴ C)	Soil 4 (⁵¹ Cr)	Soil 5 (⁵¹ Cr)	Sum A	Ranking	Manure soil	Feed soil	Sum B	Ranking
Co4	5	1	2	7	2	17	1	10	8	35	5
Co1	1	2	3	10	4	20	2	1	4	25	1
Co2	2	8	1	6	3	20	2	6	5	31	3
J2	3	3	6	1	8	21	4	5	7	33	4
Co3	9	7	4	3	1	24	5	4	2	30	2
C3	4	5	7	2	7	25	6	7	5	37	6
J3	10	9	5	5	5	34	7	9	10	53	9
C2	6	4	9	9	9	37	8	3	3	43	8
J1	8	10	10	4	6	38	9	2	1	41	7
C1	7	6	8	8	10	39	10	8	9	56	10

was relatively repellent to the manure soil (402 RLU in average).

In the biochemical ATP method, the first cleaning cycle removed a significant part of the manure soil from all surfaces (Fig. 3), but except the material C3 did not lead to the cleanness level of the unsoiled surfaces (Fig. 3). All materials except C3 behaved similarly. In removal of the manure soil, the second cleaning cycle decreased the ATP content of the surfaces approximately to the same level as before soiling. The ATP content of the surfaces soiled with the feed soil decreased after the first cleaning cycle to the same level as before soiling or even lower (Fig. 3). Material differences were negligible. In accordance with these results, there was a significant correlation between the ATP amounts of manure and feed soils after the second cleaning cycles ($r = 0.811$). In addition the ATP amount of feed soil after the first cleaning cycle correlated significantly with the soil residues of radiochemical model soil 3 (chromium oxide and triolein labelled with ¹⁴C) ($r = -0.639$).

When surfaces were divided into three groups (non-coated concretes, coated concretes and joint materials) the surface type was found to affect the cleanability of radiochemical oil model soil (soil 3, $p = 0.004$), feed soil labelled with ⁵¹Cr (soil 5, $p = 0.010$) and the ATP amount of manure after the first cleaning (soil 7, $p = 0.031$).

Contact angles

The contact angles of water in the surfaces varied between 19° and 84° (Table 6). The variation in contact angle values was wide due to the different compositions of materials. Surface type affected the water contact angles ($p = 0.050$ in comparison between non-coated concretes, coated concretes and joint materials). The contact angles of C2 and J3 were the lowest and those of Co4 the highest. Materials C1 and C3 were such porous materials that contact angles could not be measured. Water was rapidly absorbed into these surfaces. No statistically significant correlations between contact angles and soil residues were observed.

Fig. 3. ATP contents of the surface materials before soiling and after cleaning from manure and feed soils with two cleaning cycles. Results are means (columns) and standard errors of means (\pm SE, bar) of five replicates. The lower the soil residue, the better is the cleanability result. The codes of the samples are presented in Table 2.

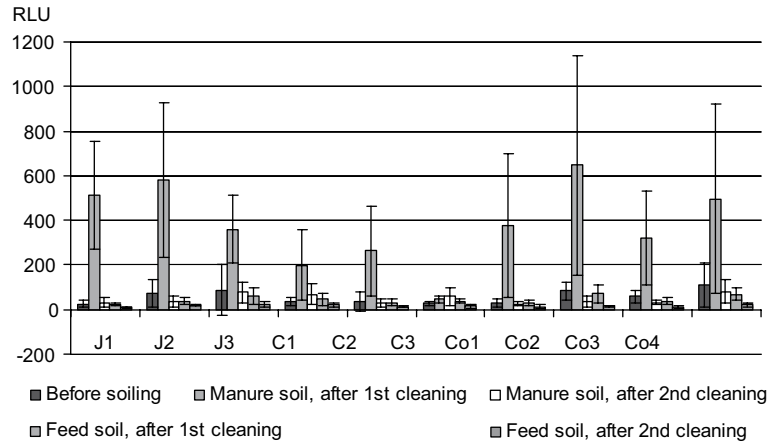


Table 6. Determined contact angles and roughness parameters as means and standard deviations (SE). Sample codes are presented in Table 2.

Code	Contact angles (°)		Roughness parameter Ra (μ m)			
			Magnification			
	Mean	SE (n=5)	20×		50×	
			Mean	SE (n=5)	Mean	SE (n=5)
J1	64	1	1.8	0.2	4.4	0.4
J2	78	2	1.0	0.2	10.5	0.8
J3	46	2	3.3	0.3	7.7	0.6
C1	-	-	2.1	0.1	5.0	0.2
C2	19	1	1.5	0.03	1.1	0.02
C3	-	-	3.0	0.1	2.3	0.2
Co1	63	2	0.9	0.06	0.4	0.01
Co2	65	2	0.2	0.04	0.5	0.05
Co3	63	3	2.2	0.3	0.7	0.08
Co4	84	2	3.7	0.1	1.8	0.3

- no result obtained due to porous surface

Topography

The linear profiles were calculated from magnifications 20 \times and 50 \times (Table 6). In the case of the 50 \times magnification Co1, Co2 and Co3 were the smoothest surfaces and J2, J3 and C1 the roughest ones. The roughness parameters R_a varied between 0.39 and 10.47 μ m. In the case of 20 \times magnification Co1, Co2 and J2 were the smoothest and Co4, J3 and C3

the roughest. The roughness parameters R_a varied between 0.18 and 3.70 μ m. The R_a -values of 20 \times magnification correlated significantly with the ATP amount of manure soil after the second cleaning cycle (Pearson's correlation coefficient $r = 0.794$). There were also statistically significant differences between the R_a -values of the three material groups

in the case of 50× magnification ($p = 0.044$). However, no other correlations were observed between surface properties and soil residues.

Qualitative SEM micrographs of different types of surface materials are presented in Fig. 4 and 5. The most typical images were selected from the replicate measurements of magnification at 500×. The cement-based joint material (J1) and cement paste, trowelled surface (C1) were porous and uneven (Fig. 4a,d). On the cement-based joint material with additives (J2) there were cracks, which might have affected the cleaning of this surface (Fig. 5b). The commercial clinker joint material (J3) was uneven, with crystals on the surface (Fig. 4c). The treated cement pastes (C2 and C3) were rougher than most of the plastic coatings (Fig. 4e,f, Table 6) but smoother than the untreated cement paste (C1) (Fig. 4d). The acrylic-coated cement paste surface (Co1) was smooth (Fig. 5a and Table

6). The polyurethane- and epoxy-coated surface materials (Co2 and Co3) were also rather smooth, whereas the surface of the polyester coating (Co4) was somewhat uneven and rough (Fig. 5b,c,d).

Discussion

In the experimental design of the study several methods from other fields of material research were implemented. This is important since there were only few previous studies available concerning surface materials and research methods in the cattle barn environment.

According to the present radiochemical study, coating improved the cleanability of materials, which is in accordance with previous studies by

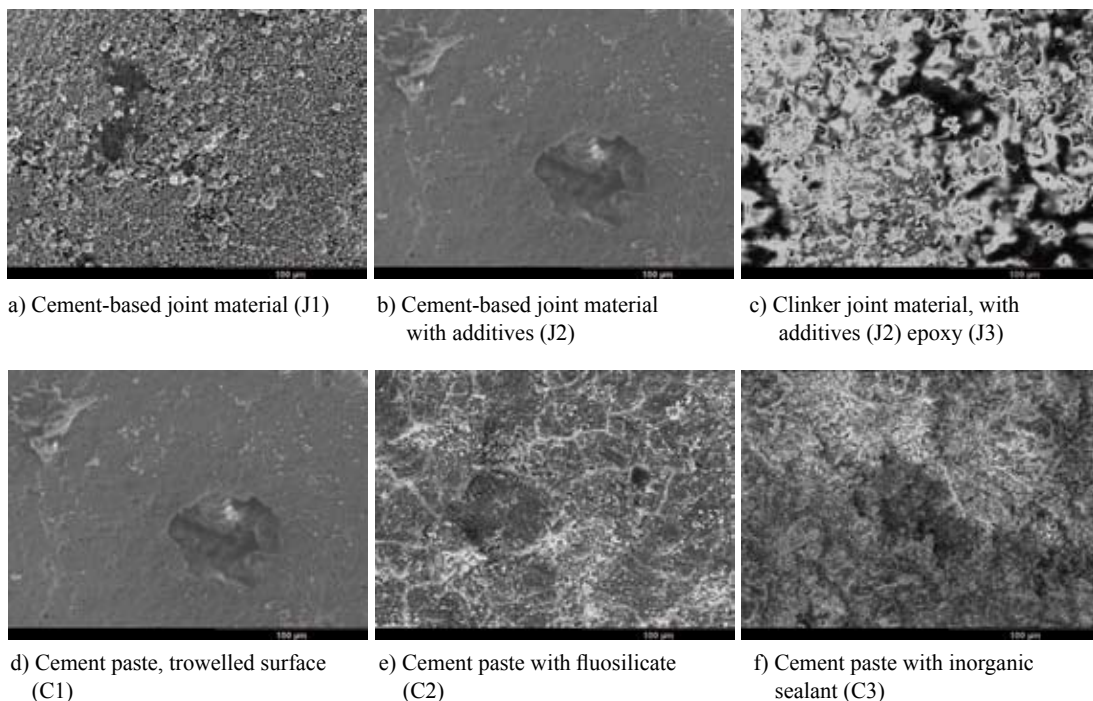


Fig. 4. SEM micrographs of surface materials (a-f), magnification 500×. The codes of surface materials are given in Table 2.

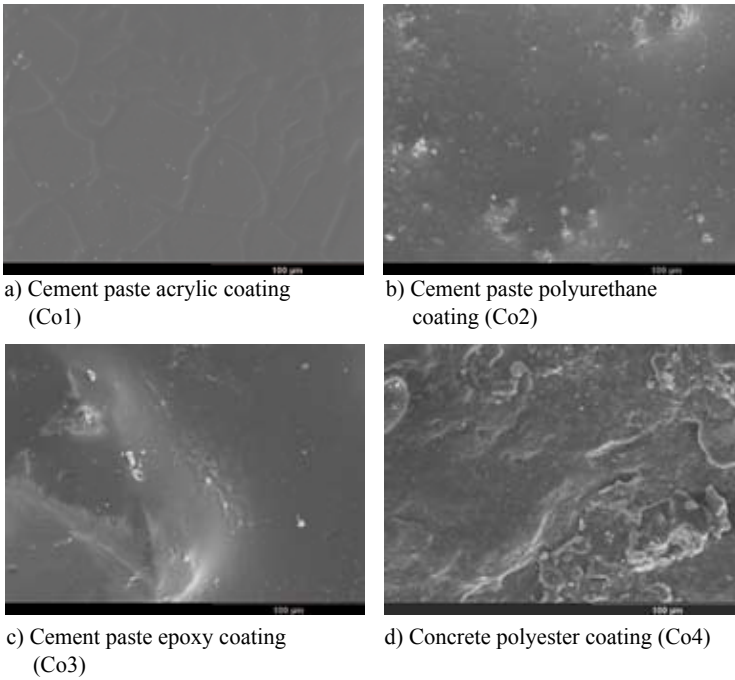


Fig. 5. SEM micrographs of surface materials (a-d), magnification 500×. The codes of surface materials are given in Table 2.

Puumala and Lehtiniemi (1993) and Kymäläinen et al. (2007). The cleanabilities from radiochemical oil model soil and labelled feed soil were both improved by coatings but no statistically significant correlations were observed, probably due to the wide variation of compositions of materials. However, the ATP amount of feed soil correlated statistically significantly with the soil residues of radiochemical oil model soil. Due to improved cleanability it is justified to use coatings where a good hygienic level is needed in cattle barns. The ATP method is a sensitive method and is valuable in the evaluation of hygienic level with non-visible soils. This was illustrated in the present study in the cases when cleaned sample surfaces looked clean (e.g. samples Co1, C2, Co4) but had high ATP levels, or looked dirty (e.g. samples J1, J3, C3) but had a relatively low ATP content. The ATP method has limitations compared with the radiochemical methods, since although the manure soil was spread well on most samples, it was

absorbed into some porous surfaces, e.g. samples C1, C2 and Co2.

In a study by Kempainen et al. (2002), epoxy as an additive improved the cleanability of joint materials from a sebum (fat)-based model soil. In accordance with this result, in our study the epoxy joint was cleaned most efficiently from oil model soil, although the cleanabilities of other model soils were poorer than those of other joint materials. This is probably due to the lower contact angle of epoxy joint. The contact angles of the non-coated concrete materials were hard to measure due to rapid absorption of water into the surface. The samples coded C1 and C3 could not be measured. The concrete was probably so porous that the liquid soaked into it directly. Coatings probably filled the holes of surfaces, and due to this they became more sealed.

The variation of roughness parameters was relatively high, coated surfaces being smoother than non-coated concretes. There were differences

between roughness values of 20× and 50× magnification. This is probably due to the different measuring areas. The 50× magnification illustrated more the micro structure of the surface, whereas 20× magnification illustrated the macro structure. The smoothing effect of coating was shown in the SEM-figures.

Radiochemical determination methods have earlier been used to evaluate cleanability of PVC model materials and ceramic tiles (Pesonen-Leinonen et al. 2006, Määttä et al. 2007a, 2007b). Except in the study by Kymäläinen et al. (2008), such determination methods have not earlier been used to evaluate concrete materials. The radiochemical inorganic model soil (soil 1) was removed more efficiently from surfaces than radiochemical organic particle or oil model soils (soils 2 and 3). The radiochemical model soils did not correlate with the radio labelled natural soils. The model soils are labelled to model one component of soil, whereas the present real soils were more complex, containing various components. The use of model soils provides detailed information concerning individual soil components, but according to this study it cannot be used to simulate natural agricultural soils. There is no previous published information concerning the use of isotope labelling with manure or feed soil. In the case of radio labelled natural soils, the results concern the labelled isotope in manure or feed mixture, but indicate the behaviour of the whole soil mixture. From the practical point of view, addition of isotope to the bulk soil was the only way to label the manure and feed soil in this study. However, in our earlier study radiochemical model soils correlated with manure soil when the cleanability was determined by colorimetry (Kymäläinen et al. 2008). In the present study correspondence was observed between radiochemical oil model soil and the ATP amount of feed soil after the first cleaning cycle.

There is no previous published information concerning use of the ATP method with manure or feed soil. Since both microbial and non-microbial (somatic) cells contain ATP and thus all material of cellular origin gives a response with the ATP bioluminescence method (Green et al. 1999), both microbes and other organic matter in the manure

soil probably resulted in its high ATP content. Furthermore, the reproduction of microbes on the surface both after soiling and after cleaning may have affected the ATP results. However, with the present experimental setup it was not possible to analyse in more detail the effects of different components of the soil on the ATP results. In general it is known that one ATP molecule produces one photon of light, and thus the light intensity from the reaction is proportional to the amount of ATP in the sample (Green et al. 1999). The ATP method is normally used for detection of surface contamination (Davidson et al. 1999, Storgårds 2000, Champiat et al. 2001, Wirtanen et al. 2002, Redsvén et al. 2007), and on the basis of these studies from other fields of application, the method was tested on agricultural surfaces and soils in the present study.

Using the biochemical ATP method the differences between the non-coated concrete and coated concretes were less clear than in the radiochemical study. This is probably due to the disadvantage that the biochemical ATP determination method does not take into account the amount of absorbed soil. The biochemical ATP method is sensitive to organic contaminants and therefore useful in determination of cleanability at sites or rooms with relatively high hygienic requirements, e.g. in milk rooms.

In the present study the oil-containing radiochemical model soil was removed the least efficiently and the inorganic particle soil containing chromium oxide the most efficiently. These results from concrete materials in the radiochemical study were mainly consistent with the results of our earlier studies concerning plastic and ceramic materials (Määttä et al. 2007a,b). By examining the cleanability and surface properties of laboratory-made and commercial surface materials intended for use in cattle barns it was possible to select some promising surfaces for a pilot study in a cattle barn. The materials selected for the pilot study were epoxy-, polyurethane- and acrylic coatings for floorings, and in addition the traditional concrete and polyester coating were selected for the feeding table.

Conclusions

In general, coatings improved the cleanability of the flooring materials according to the results of the radiochemical determination method. In other words, polyester, acrylic and polyurethane coatings were cleaned the most efficiently and the cleanabilities of the non-coated concretes were poorest. In general, the epoxy-coated concrete was cleaned the most efficiently from the labelled natural soils, manure and feed. According to both radiochemical measurements, the cleanability of the non-coated concrete including inorganic sealant from manure soils was good. The cement-based joint materials were cleaned better than the joint containing epoxy especially from the inorganic particle soil, but less efficiently from the oil model soil and labelled feed soil. According to both contact angle measurements and topographic measurements, the coatings sealed the porous surfaces.

In the present experimental setup, both the radiochemical and the biochemical ATP determination methods were suitable for examining cleanability of concrete materials from agricultural soils. Only the radiochemical determination provides detailed quantitative results, but its use is limited to laboratory studies. A correlation was observed between the results of cleanability of radiochemical oil model soil and the ATP amount of feed soil after the first cleaning.

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SELOSTUS

Laboratoriotutkimus navetan uusista ja perinteisistä pintamateriaaleista

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Tutkimuksen tavoitteena oli selvittää seitsemän erilaisen betonimateriaalin koostumuksen ja pinnoitteen vaikutus niiden puhdistuvuuteen. Lisäksi tutkittiin kolmea erilaista saumausainetta. Pintaominaisuudet selvitettiin kontaktikulmamittarilla, optisella profilometrillä ja pyyhkäisyelektronimikroskoopilla (SEM). Puhdistuvuutta mitattiin radiokemiallisilla määritysmenetelmillä sekä biokemiallisella menetelmällä, joka perustuu ATP:n (adenosiinitrifosfaatti) määrän mittaamiseen. Likoina käytettiin laboratoriotutkimuksiin kehitettyjä mallilikoja ja luonnollisia maatalouden likoja. Sekä radiokemialliset määritysmenetelmät että ATP-menetelmä soveltuivat maatilalikojen puhdistuvuuden sekä likajäämien määrittämiseen pinnoilta. Radiokemialliset menetelmät antavat kvantitatiivisen tuloksen, mutta niitä voidaan käyttää ainoastaan laboratorio-olosuhteissa.

Pinnoittamattomien ja pinnoitettujen betonien sekä saumausaineiden kontaktikulmat erosivat toisistaan. Karheusarvojen ja SEM-kuvien perusteella saumausaineet olivat karheimpia pintoja ja pinnoittaminen tasoiitti betonipintoja. Radiokemiallisten puhdistuvuuskokeiden mukaan pinnoittaminen paransi myös puhdistuvuutta. ATP-menetelmällä ainoastaan tiivistetty betoni erosi muista materiaaleista; se puhdistui lantaliasta parhaiten ensimmäisen puhdistuksen jälkeen. Epoksipohjainen saumausaine puhdistui öljymäisestä malliliasta parhaiten, kun saumausaineita verrattiin keskenään. Kokonaisuutena polyesteri-, akryyli- ja polyuretaanipinnoitetut näytteet puhdistuivat parhaiten. Pinnoittamista suositellaan tiloihin ja pinnoille, joilta vaaditaan hygieenisyyttä, esimerkiksi ruokintapöydille ja lypsyasemille.