Kaolin, bentonite, and zeolites as feed supplements for animals: health advantages and risks

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ABSTRACT: Feeding kaolin as a supplement to pigs for prevention of diarrheal diseases has been introduced into some farms in the Czech Republic. Peat was used in the 1990s for a similar purpose; however, most farmers ceased feeding peat as a supplement because of its frequent contamination with conditionally pathogenic mycobacteria, esp. with *Mycobacterium avium* subsp. *hominissuis*. The aim of the present paper is to review available literature from the standpoint of the advantages and disadvantages related to feeding kaolin as a supplement to animals. Its positive effects exerted through the diet primarily consist in its adsorbent capability which may be useful for detoxification of the organism and for prevention of diarrheal diseases in pigs. Because the mechanism of action of kaolin fed as a supplement is unknown, a risk related to its potential interactions with other nutrient compounds of the diet exists. Therefore, it is necessary to investigate the effectiveness and safety of feeding kaolin in detail with regard to the health status and performance of each farm animal species. The disadvantage of kaolin use is its potential toxicity, provided it has been mined from the environment with natural or anthropogenic occurrence of toxic compounds. Another risk factor is a potential contamination of originally sterile kaolin with conditionally pathogenic mycobacteria from surface water, dust, soil, and other constituents of the environment in the mines during kaolin extraction, processing and storage.

Keywords*:* kaolinite; phyllosilicate; geophagy; toxic compounds; zoonoses; parasites; tuberculosis; pigs tuberculosis; feed safety

Contents

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1. Introduction

In late 1990s, farmers in the Czech Republic began to use non-conventional feed supplements such as peat to prevent economic losses caused by diarrhea in piglets during the periods after birth and after weaning (Matlova et al., 2003; Pavlik et al., 2003). Due to its adsorbent capability, peat alleviates the adverse effects of toxins present in feeds, and thus protects highly sensitive mucosa of the digestive tract, stomach and intestines, particularly in the young farm animals (Kuhnert et al., 1991; Lotosh, 1991; Stepchenko et al., 1991; Herzig et al., 1994; Beer and Lukanov, 1998; Beer et al., 2000; Zagorchev et al., 2000). After supplementation of peat with minerals (particularly iron), an improvement in health status has been observed in piglets (Fuchs et al., 1995).

Although underground peat is sterile after the extraction (Kazda, 2000), peat as a supplement may be subsequently contaminated with conditionally pathogenic mycobacteria, which have likewise been isolated from tuberculous lesions of pigs (Matlova et al., 2004a,b). Due to the increased occurrence of tuberculous lesions in herds of pigs fed peat as a supplement in the Czech Republic during the years between 1998 and 1999, the farmers ceased feeding peat as a supplement (Pavlik et al., 2003).

Accordingly, a search has been initiated to identify a raw material with lower contamination risks, but similar dietary effects. Mining of kaolin deposits in southern Moravia, Czech Republic, has prompted some Czech farmers to experiment with kaolin. As kaolin feeding showed to be effective in some farms (Matlova et al., 2004c), the abundance and efficacy of kaolin may provide a suitable material to protect livestock from diarrheal diseases. The purpose of the present review is to analyse the characteristics of kaolin and its use in animal or human nutrition.

2. Kaolin availability

2.1. Kaolin deposits in the Czech Republic

Kaolin is formed under acidic conditions through weathering or hydrothermal changes of feldspars, and – to a lower extent – also other aluminosilicates. It can form independent weathered kaolin deposits, kaolinite clays or may be a compound of kaolinite sandstones and oolitic ironstones, and less frequently also of pegmatites and hydrothermal deposits. The most significant kaolin deposits were formed through intensive weathering of rocks rich in feldspar (granite, arkose, certain types of ortho-gneisses, and migmatites). Millions years ago, original material was decomposed by weathering, giving rise to kaolin and silica combined with higher or lower amounts of admixtures. Mechanical erosion formed the rock under the tropical climate of that era and at increased temperatures, chemical corrosion occurred under the activity of water saturated with CO_2 and humic acids which eluted from water (Bernard and Rost, 1992; Slivka, 2002).

World renowned deposits in the Czech Republic are especially situated in the district of Karlovy Vary (Sedlec, Podlesi, and Otovice). Kaolin deposits in the area of Karlovy Vary are primary, i.e. kaolin remained in the place of its formation. Extracted raw material contains 20 to 30% kaolin; the remainder is silica sand which is an integral part of the raw material. Deeper deposits tend to be less kaolinized. Larger areas with kaolin matter contents of 15 to 35% formed through weathering of arkoses are found in the vicinity of Horni Briza, Kaznejov, and Chotikov. Lower quality kaolin deposites are near Nova Role, Vidnava, Kadan, Podborany, Znojmo, and Veverska Bityska (Kourimsky, 1957; Pauk et al., 1962; Stejskal, 1971; Duda et al., 1990; Bernard and Rost, 1992; Slivka, 2002).

2.2. Kaolin mining and processing ("mine U-ZN" in southern Moravia)

Kaolin was obtained from extracted kaolinite or kaolinite-illitic gritstone or pudding-stone from the "mine U" in southern Moravia using the following procedure (unpublished data):

1. Superficial soil layer (about 50 cm) was removed, and the raw material was floated to a suction pump by water cannon (water source was a pond formed on the surface of the mine after kaolin extraction).
2. It was transported in the form of dense slurry through about 150 m long pipeline with about 20 cm in diameter to the processing plant halls.
3. After kaolin washing, classification and separation steps according to the particle size, kaolin sedimentation, addition of colloid agent, and kaolin drying in wire baskets, the product was finished and could be dispatched to customers.

3. Kaolin characteristics

3.1. Kaolin structure

Kaolin is a plastic raw material, particularly consisting of the clay mineral kaolinite. The chemical formula is $Al_2O_3.2SiO_2.2H_2O$ (39.5% Al_2O_3, 46.5% SiO_2, 14.0% H_2O). In systemic mineralogy, kaolinite ranks among phyllosilicates, which are stratified clay minerals formed by a net of tetrahedral and octahedral layers. Phyllosilicates are classified into the main groups according to the type of the layers, interlayer content, charge of the layers and chemical formulas. Besides kaolinite groups, serpentine, halloysite, pyrofylite, mica, and montmorillonite groups also rank among phyllosilicates. Group of kaolinites includes di-octahedral minerals (1:1) with two layers, one silica [SiO_4] tetrahedral layer and one aluminium [$Al_2(OH)_4$] octahedral layer. The layers are bonded together by sharing oxygen anion between Al and Si. Together, these two layers are called platelets (Pauk et al., 1962; Stejskal, 1971; Bailey, 1980; Duda et al., 1990; Bernard and Rost, 1992; Bish, 1993; Klein and Hurlbut, 1993; Slivka, 2002).

3.2. Physical properties

The 1:1 platelets of kaolinite are held together strongly via hydrogen bonding between the OH of the octahedral layer and the O of the tetrahedral layer. Due to this strong attraction these platelets do not expand when hydrated and kaolinite only has external surface area. Also, kaolinite has very little isomorphic substitution of Al for Si in the tetrahedral layer. Accordingly, it has a low cation exchange capacity. Kaolinite easily adsorbs water and forms a plastic, paste-like substance (Duda et al., 1990; Bernard and Rost, 1992; Klein and Hurlbut, 1993; Slivka, 2002).

4. Kaolin in the diet fed to farm animals

4.1. Decontaminating properties of kaolin

Due to its adsorbent capability and lack of primary toxicity, kaolin is considered a simple and effective means to prevent or ameliorate the adverse effects exerted by many toxic agents, not only those from the environment, but also those from the living organisms. Kaolin based medication often combined with pectin is commonly used as a palliative for diarrhea and digestive problems in humans (Heimann, 1984; Kasi et al., 1995; Gebesh et al., 1999). Kaolin, given to the animals in the diet, firmly and selectively binds compounds present in the diets which are noxious to the intestine and thus decreases their absorption through intestinal mucosa into the organism and subsequently prevents their toxic mode of action. A number of studies confirmed kaolin capability to decontaminate aflatoxins (Abdel-Wahhab et al., 1999; Phillips, 1999), plant metabolites (alkaloids, tannins), diarrhea causing enterotoxins (Dominy et al., 2004), pathogenic microorganisms, heavy metals (Hassen et al., 2003; Katsumata et al., 2003) and poisons (Knezevich and Tadic, 1994). In contrast, vitamin B_{12} adsorption by kaolinite clays is very low (Hashsham and Freedman, 2003).

4.2. The other effects of kaolin feeding

Few studies have investigated the effects of kaolin-feeding on farm animals. Savory (1984) investigated the effect of kaolin feeding on adult roosters. That author did not register any change in the live body weight gain when 100 and 200 g kaolin/kg of the diet was fed. Although in the initial phase of the experiment when animals ingested 300 g kaolin/kg of the diet their weight did not increase, and when the animals ingested 400 g kaolin/kg of the diet, the live body weight of the animals even decreased; the differences were gradually compensated, primarily by increased feed intakes. Although it was not possible to completely compensate the body weight differences by increased feed intake, compensation was reached by significant increase in digestibility of basal diet. That effect was observed in a group fed 100 g kaolin/kg of the diet within a couple of days when more than 200 and 300 g of kaolin per week and 400 g per three weeks, was consumed, respectively. Sakata (1986) registered stimulation of the live weight gain in rats given kaolin combined with the diet (100 mg/g) with concurrent proportional increase in the weight of the tissues of some digestive organs.

5. Geophagy

Geophagy is the deliberate consumption of unpalatable soils, particularly clays with high content of kaolin. It has been observed not only in animals, but also in the human population (Johns and Duquette, 1991; Mahaney et al., 1996; Knezevich, 1998). Kaolinites are the most common soil minerals which together with other clay minerals and organic matter form the topsoil complex. Various hypotheses have been advances to explain geophagic behaviour (Wilson, 2003):

(i) Detoxification of noxious or unpalatable compounds present in the diet,
(ii) Alleviation of gastrointestinal upsets such as diarrhea,
(iii) Supplementation of mineral nutrients,
(iv) Alleviation of excess acidity in the digestive tract.

5.1. Geophagy in human population

Geophagy in human population has particularly been registered in children (Geissler et al., 1998a; Saathoff et al., 2002) and in pregnant women (Patterson and Staszak, 1977; Geissler et al., 1998b, Prince et al., 1999; Sapunar and Fardella, 1999). Gastrointestinal adsorption of plant metabolites and enterotoxins is considered the most reasonable underlying cause of geophagy in humans (Dominy et al., 2004).

5.2. Geophagy in animal population

Geophagy is sometimes considered in other primates, is generally viewed as an adaptable behavior (Dominy et al., 2004). Geophagy was observed in 76% of free living monkeys *Macaca mulatta*. The earth consumed by the animals contained high levels of kaolinite clays. Subsequently, it was found that despite a high infestation of the monkeys with one or more types of endoparasites (89% animals), prevalence of diarrheal diseases was very low and reached only 2% (Knezevich, 1998). Adsorption of toxic, unpalatable compounds from the diet and alleviation of diarrhea were likely the main reasons of consumption of soil with a rather high contents of kaolin (< 20%) by cattle (Mahaney et al., 1996). Geophagic behaviour of free living birds leads to reduction of biological absorption of toxic agents (particularly alkaloids and tannins) particularly present in the seeds and various fruits (Diamond et al., 1999; Gilardi et al., 1999).

Kaolin intake is also commonly observed in rats suffering from acute diseases (Burchfield et al., 1977; Mitchell et al., 1977a,b; Morita et al., 1988; Davey and Biederman, 1998), gastrointestinal disorders (Mitchell et al., 1977a; McCaffrey, 1985), arthritis and stress (Burchfield et al., 1977). Vomiting (*emesis*) appears to be a functionally similar defence behavior in humans and other animals (Morita et al., 1988; Takeda et al., 1993). Experimental groups of rats infected with devitalised *Mycobacterium butyricum* (*M. smegmatis*, according to the currently accepted taxonomy; Wayne and Kubica, 1986) in the form of mineral oil suspension, consumed statistically significantly more kaolin than the control group of rats (Burchfield et al., 1977; Wayne and Kubica, 1986).

5.3. Supplementary theory of geophagy

The opinion on the effect of geophagy on supplementation of the organism with minerals is not uniform. Clinical studies showed that geophagy on one hand alleviated (Danford, 1982; Danford et al., 1982) and on the other hand caused mineral deficiency (Halstead, 1968). Geophagy may be associated with anaemia occurrence and iron deficiency. Significant reduction in levels of haemoglobin and haematocrit and erythrocyte counts with consequent induction of maternal anaemia was observed during investigation of the effect of kaolin on blood parameters and embryonic development in gravid rats. Marked decrease in the birth weight of the young was likewise recorded. In contrast, the intake of kaolin supplemented with iron resulted in normal levels of haemoglobin, haematocrit and erythrocyte counts and birth weight of the young (Patterson and Staszak, 1977). Other authors (Geissler et al., 1998b) emphasized the adverse effect of geophagy on haemoglobin and serum ferritin (high iron level proteins) levels. They believe that consumption of clay soil substances are the important sources of iron and other minerals in the diet, such as calcium, sodium, phosphorus and zinc (Vermeer, 1966; Hunter, 1973; Hunter and De Kleine, 1984; Kreulen and Jager, 1984; Johns and Duquette, 1991; Abrahams, 1997; Geissler et al., 1998b).

Varied results obtained in different studies seeking to confirm the nutrient supplementation hypothesis of geophagy have likely been based on different chemical and mineralogical composition of geophagic materials (Wilson, 2003). Clay is a natural composite material with substantial proportion of phyllosilicates. Clay mineral contents detected by mineralogical analysis of geophagic soils range is between 20 and 90% with dominant contents of kaolinite and lower proportions of smectite, illite, and halloysite (Johns and Duquette, 1991; Wilson, 2003). Although kaolinite was found to be the dominant mineral by most of the studies dealing with geophagy, the term "kaolin" is used non-specifically in many of them. However, general chemical and mineralogical analyses are of little relevance for clarification of the nutrient supplementation hypothesis (shared by many studies) unless supported by physiologically based extraction tests (Wilson, 2003).

6. Alternative feed supplements of similar qualities added to animal diets (bentonites and zeolites)

6.1. Bentonites

6.1.1. Composition of bentonites

Bentonites are clays with prevailing montmorillonite of the smectite group, and can be considered alternative raw materials. Their good capability to bind water and mineral nutrients and protect them from washing up is a useful prerequisite for enhancement of soil fertility (Stejskal, 1966). In contrast to kaolin with a simple stratified structure which allows adsorption to the surface layer only, three layer structure complexes of montmorillonite allow also internal absorption of ions into the interlayer sheets to redundant non-saturated charges of the layer complex. Whereas in kaolinite, neither interlayer molecular water, nor exchangeable cations are found, which results in a relatively low cation exchange capacity, the interlayer space of montmorillonite is occupied by easily exchangeable ions of different types. Prevailing cation exchangers significantly affect bentonite features. Modified forms (monoion forms, intercalated with organic or inorganic cations) of natural montmorillonites (bentonites) are used in a number of technological applications. Their applications are being investigated nowadays; however, it is clear already now that they are the materials of nutrition which can be, without exaggeration, termed as materials of the new millennium (Slivka, 2002).

6.1.2. Adsorbent capability of bentonites

High adsorbent capability of smectite minerals have found wide-range applications not only in industry, but also as excellent adsorptive materials of heavy metals and bacteria (Hassen et al., 2003; Katsumata et al., 2003) and toxic and antinutritive agents (Ditter et al., 1983; Schell et al., 1993a,b; Pulsipher et al., 1994; Abdel-Wahhab et al., 1999; Ibrahim et al., 2000; Phillips et al., 2002). Bentonites in animal diet act as gut protectants (enterosorbents), which rapidly and preferentially bind aflatoxins from the digestive tract and thus reduce their absorption into the organism (Grant and Phillips, 1998; Phillips et al., 2002). In that manner, adverse effect of aflatoxins on efficiency and liver function is minimized without marked defects in mineral metabolism of the animals (Schell et al., 1993a,b; Santurio et al., 1999).

6.1.3. Comparison of adsorbent capability of bentonites and kaolin

In the tests of capability of various adsorbents to bind toxins, bentonites showed the best results, followed by kaolin-pectin (Kaopectate). Kaolin alone was less effective (Ditter et al., 1983). Bentonite supplementation (5%) of the diet given to chickens fed different-type nutrient deficient diets (e.g. deficiency in macroelements, microelements, vitamins and proteins) can enhance the feed intake by the chickens, and the weight gains which may be decreased by these deficiencies (Southern et al., 1994).

6.2. Zeolites

6.2.1. Composition of zeolites

Zeolites are natural and synthetic hydrated crystalline aluminosilicates endowed with ion exchanging properties. Among a high number of natural zeolites, clinoptilolite is best known. In the Czech Republic, no economically utilizable deposits have been detected. Zeolites are classified as tectoaluminosilicates with large pores and channels in the structures containing loosely bound water molecules (so called zeolite water) and alcalic cations (Na^+, K^+, Li^+, Cs^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Sr^{2+}). They can selectively adsorb gas and steam molecules, reversibly adsorb and desorb water, or based on ion selectivity they can exchange own cations for other ones (Boranic, 2000; Melenova et al., 2003).

6.2.2. The use of zeolites in human and animal nutrition

Zeolites, kaolin and alike bentonites, are also used as effective adsorbents of toxic agents, particularly aflatoxins from the feeds (Parlat et al., 1999; Phillips, 1999; Oguz and Kurtoglu, 2000; Ortatatli and Oguz, 2001; Rizzi et al., 2003). They effectively minimize adverse effects of aflatoxins on feed intake, performance and nutrient conversion (Parlat et al., 1999; Oguz and Kurtoglu, 2000) and reduce mycotoxin concentration in the livers of affected animals (Rizzi et al., 2003). A lower concentration (15 g/kg) of zeolite in the diet seems more effective than a higher concentration (25 g/kg) as it was described by Oguz and Kurtoglu (2000).

Zeolite supplemented diets are well tolerated by the animals; they support biomass production and improve the health status of the animals (Martin-Kleiner et al., 2001; Papaioannou et al., 2004). Statistically significant improvement of feed conversion after clinoptilolite feeding (2% of the diet) to piglets in the period from weaning to slaughter was observed (Papaioannou et al., 2004). Concomitant administration of clinoptilolite and antibiotics (enrofloxacin and salinomycin) resulted in less severe forms of post weaning diarrhea syndrome, witch had a shorter clinical course, decreased mortality in the period of weaning and positive effect on the pig weight gains in respective phases of fattening. Clinoptilolite in the diet for layer hens (50 g/kg) increased the numbers of laid eggs, stability of eggshell and efficiency of food utilisation; however, neither the onset of the egg lay cycle, nor the egg weight were affected (Olver, 1997). Moreover, zeolite supplementation of the diets with high contents of cholesterol exerts hypocholesterolemic effect (Sorokina et al., 2001).

Zeolites are amphoteric, hence partly soluble in acid or alkaline media; but their solubility is generally low within the physiological pH range. Minimal amounts of free aluminium from the ingested zeolite are resorbed from the gut (Boranic, 2000). Rabon et al. (1995) recorded significant increase in aluminium and zinc serum concentrations in laying hens, which can be associated with improved quality of the eggshell and bone development. Martin-Kleiner et al. (2001) did not find any alteration in blood sera of experimental animals fed zeolite, except 20% increase in potassium level. Erythrocyte, haemoglobin and platelet levels have not been altered either. In contrast, Enemark et al. (2003) recorded initial slight decline in calcium concentrations in sera and urine of dairy cows fed diet supplemented with zeolite which was likely caused by decreased availability of calcium from the zeolite containing diet. The decrease in dairy cow serum concentrations of phosphorus and magnesium was partly caused by interference of zeolite with intestinal absorption and partly by a marginal dietary supplementation of these minerals.

Zeolites ingested with the diet lead to the shift of pH and buffering capacity of gastrointestinal secretions, affect the transport through the intestinal epithelium, composition of intestinal bacterial flora and resorption of bacterial products, vitamins and microelements. Increasing therapeutic use of encapsulated zeolite powders enriched with vitamins, oligoelements or other physiologically important ingredients for oral administration has been recorded (Boranic, 2000).

6.2.3. The use of zeolites for ammonia adsorption

Besides the use in the industrial sector, food industry and ecology, zeolites found application in removal of excess ammonia both in the digestive tract (feed supplement) and bedding (Boranic, 2000; Meisinger et al., 2001; Melenova et al., 2003).

7. Toxicological impact of kaolin

After oral or intradermal administration of kaolin, no toxic effects were observed in the organisms (Anonymous, 1998). Phyllosilicates are used as anticaking agents added to diets (Grant and Phillips, 1998). The use of kaolin in foodstuffs designated as E 559 has been permitted by Decree No. 54/2002 Coll. of the Czech Republic.

7.1. The risk of kaolin contamination with dioxins

Contamination of kaolin with dioxins represents a potential risk. In the year 1997, Food and Drug Administration (FDA) in the USA detected increased contamination of poultry meat samples with PCDD/PCDF (polychlorinated dibenzodioxins and polychlorinated dibenzofurans); the sources of the contamination were clay minerals (kaolin, bentonites, and zeolites) used as anti-caking agents in the diets. Later on, a similar contamination with PCDD/PCDF was also detected in Europe (Abad et al., 2002; Eljarrat et al., 2002; Schmid et al., 2002).

7.2. The risk of kaolin contamination with mycobacteria

Several risk factors which may cause kaolin contamination, particularly with conditionally pathogenic mycobacteria, during its production must be considered (Matlova et al., 2004c). They are often found in surface water (Horvathova et al., 1997; Kazda, 2000; Matlova et al., 2003) used for levigation during kaolin processing. If the final product is humid, and the temperature used for drying does not reach the values necessary for conditionally pathogenic mycobacteria devitalisation (Pavlas et al., 1984), the risk of induction of tuberculous lesions in the pig and cattle lymph nodes is high (Pavlik et al., 2002, 2003; Kozak et al., 2003). Although the raw material was sterile after extraction from the mine, it was subsequently contaminated with conditionally pathogenic mycobacteria from surface water from the pond (Kazda, 2000; Matlova et al., 2004c). Surface water is regarded as the most important source of conditionally pathogenic mycobacteria (Beerwerth, 1973; Kazda, 1973, 2000). Therefore, *M. avium* subsp. *hominissuis* and other non-identified species of slowly growing mycobacteria were isolated from kaolin fed to pigs as a supplement (Matlova et al., 2003, 2004c).

There may also be other sources of conditionally pathogenic mycobacteria contaminating kaolin such as dust, soil layer above kaolin deposit, bird faeces etc. (Beerwerth and Schurmann, 1969; Dawson, 1971; Beerwerth and Kessel, 1976a,b). From the standpoint of the host organism, particularly of pigs, which are the most susceptible farm animals to mycobacterial infections, contamination with both *M. a. hominissuis* and *M. fortuitum* and other conditionally pathogenic mycobacteria which may induce tuberculous lesions in the lymph nodes of pigs must be considered (Matlova et al., 2003). Especially members of *M. avium* complex (*M. a. avium*, *M. a. hominissuis*, and *M. intracellulare*) are causal agents of serious infections in animal and human populations (Dvorska et al., 1999; Pavlik et al., 2000, 2002; Dvorska et al., 2002; Lescenko et al., 2003; Pavlik et al., 2003; Machackova et al., 2003, 2004; Bartos et al., 2004; Dvorska et al., 2004; Matlova et al., 2004a,b,c,d; Pavlik et al., 2004).

8. Conclusions

Based on the data from literature concerning the positive effect of adsorbent capability not only of kaolin, but also other clay minerals (montmorillonites, zeolites), these unconventional feed supplements may be recommended for the detoxification of the organism and prevention of diarrheal diseases in animals. With respect to the fact that the use of kaolin as a feed supplement has not been well clarified, a risk related to its potential interactions with other nutritive compounds of the diet exists. Therefore, it is necessary to investigate in detail the effectiveness and safety of feeding kaolin with respect to the health status and performance of each species of farm animals. It is also necessary to prevent its potential contamination with conditionally pathogenic mycobacteria (especially *M. avium* complex) by immediate packing of kaolin in airtight bags under the field conditions, and maintaining temperature below 18°C, as conditionally pathogenic mycobacteria do not propagate under such conditions of the external environment.

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