

Slurry Acidification

Introduction

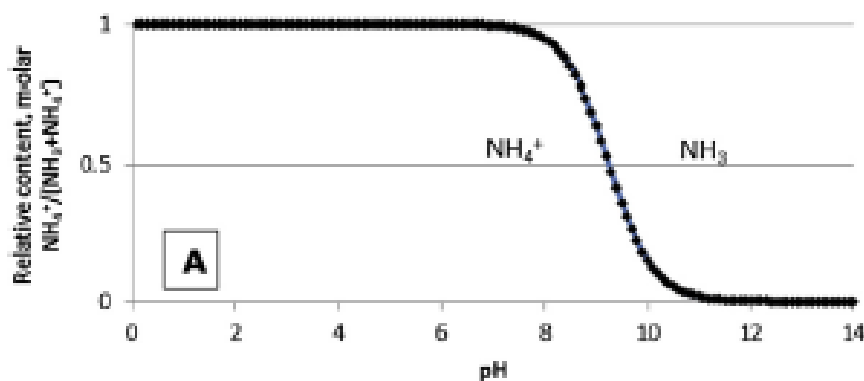
Ammonia (NH_3) is a highly reactive and soluble alkaline gas. It can originate from both natural and anthropogenic sources, with the main source being agriculture, e.g., manures, slurries and fertiliser application (APIS, 2016). Excess nitrogen causes eutrophication and has acidifying effects on semi-natural ecosystems, which in turn can lead to species composition changes and other deleterious effects. The UK has international commitments to reduce NH_3 emissions by 16% by 2030 based on 2005 levels. Northern Ireland is responsible for 12% of UK ammonia emission despite only representing 6% of the land area. The vast majority associated with manure management practises.

Ammonia is produced from the hydrolysis of urea and subsequent volatilisation of nitrogen as ammonia. Emissions and deposition vary spatially, with "emission hot-spots" associated with locations with high numbers of livestock farms. In context, ammonia is a major issue facing UK and Northern Ireland agriculture.

Ammonia emissions are a major problem associated with animal slurry management, solutions to overcome this problem are required worldwide by farmers and stakeholders. One way to minimise ammonia emissions from slurry is to decrease slurry pH by addition of acid (Fangueiro et al., 2015).

Acidification methods

Acidification has been commonly used in countries such as Denmark and its effectiveness with the ammonia (NH_3) emission mitigation has been extensively documented. The concept of reducing slurry pH to abate nitrogen losses to the air relies on the equilibrium between ammonium (NH_4^+) and NH_3 .



Graph depicting the relationship between pH and proportion of Ammonia to Ammonium.

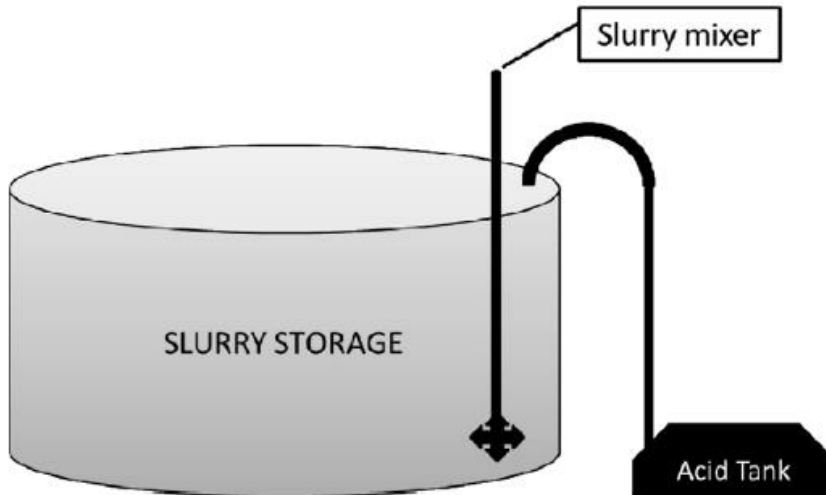
There are 3 methods of acidifying manure within the farming system which are outlined below.

(1) In house acidification

In-house acidification is considered a long-term acidification. The acid or agent is applied on a daily or weekly basis to the slurry. The slurry is pumped from the shed into a treatment tank; acid is added (with mixing) to reach set pH level. Aeration is performed simultaneously to avoid foaming. Part of the slurry is returned to the slurry channels, and part is sent to a storage tank.

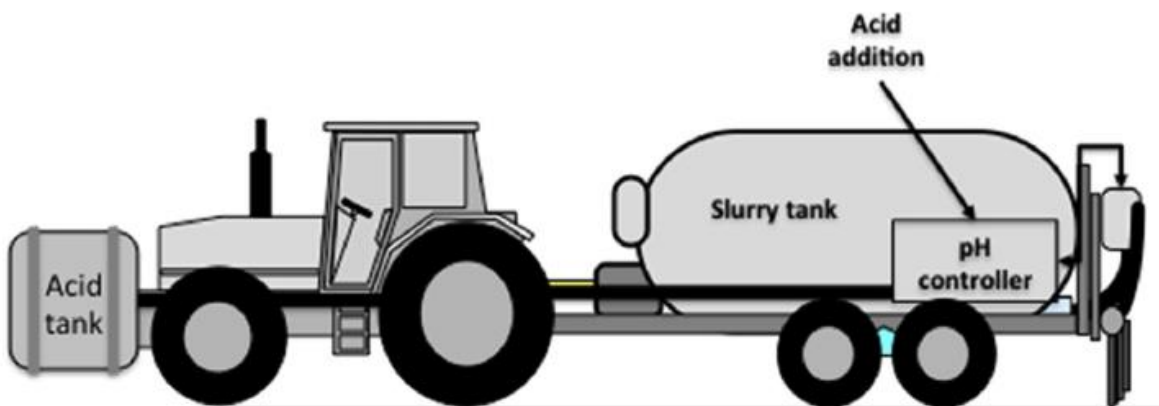
(2) Storage tank acidification

Storage tank acidification can be considered short or long-term acidification depending on its timing. The acid or agent is added to the storage tank or lagoon under heavy mixing. Foam is produced upon the addition, and its removal is the main constraint of this process. Acidification can be performed shortly before collection of the slurry for field application or several months before application however re-acidification may be necessary.



(3) Acidification at field application

Acidification at field application is considered a short-term acidification. The acid or agent is applied to the slurry immediately before crop application, in a static mixer installed in the output junction of the slurry tanker.



Ammonia, methane, and carbon dioxide are emitted during all three steps of the slurry management process: in the shed, during storage, and during or after soil application. This section will go through these gaseous emissions below.

Gas	Effect of acidification on emissions	References		
NH ₃	↘	In-house	✓ 37% with nitric acid ✓ 50–70 % with sulfuric acid	Monteny and Erisman, 1998; Kai et al., 2008; Infarm A/S, 2014a, 2014b Lefcourt and Meisinger, 2001; Shi et al., 2001; Berg et al., 2006; Kai et al., 2008 Stevens et al., 1989; Frost et al., 1990; Bussink and Bruins, 1992; Stevens et al., 1992; Pain et al., 1994; Frost, 1994; Kai et al., 2008; Biocover A/S, 2012; Nyord et al., 2013
		Storage	✓ 50–88 % with sulfuric acid ✓ 60–98% with aluminum sulfate ✓ 27–71% with other acids	
		Field	✓ 40–80% with pig slurry (different acids) ✓ 15–80% with cattle slurry (different acids)	
N ₂ O	↗	Field	✓ >100% with nitric acid ✓ 23% with sulfuric acid	Velthof and Oenema, 1993; Fangueiro et al., 2010
CO ₂	→	Storage		Fangueiro et al., 2010; Dai and Blanes-Vidal, 2013; Fangueiro et al., 2013
H ₂ S	→ / ↘ (initial burst)	Storage		Eriksen et al., 2012; Dai and Blanes-Vidal, 2013
CH ₄	↘	Storage	✓ 90% with lactic acid ✓ 40–65% with hydrochloric acid ✓ 17–75% with nitric acid	Berg et al., 2006; Berg and Papsiczki, 2006; Petersen et al., 2012

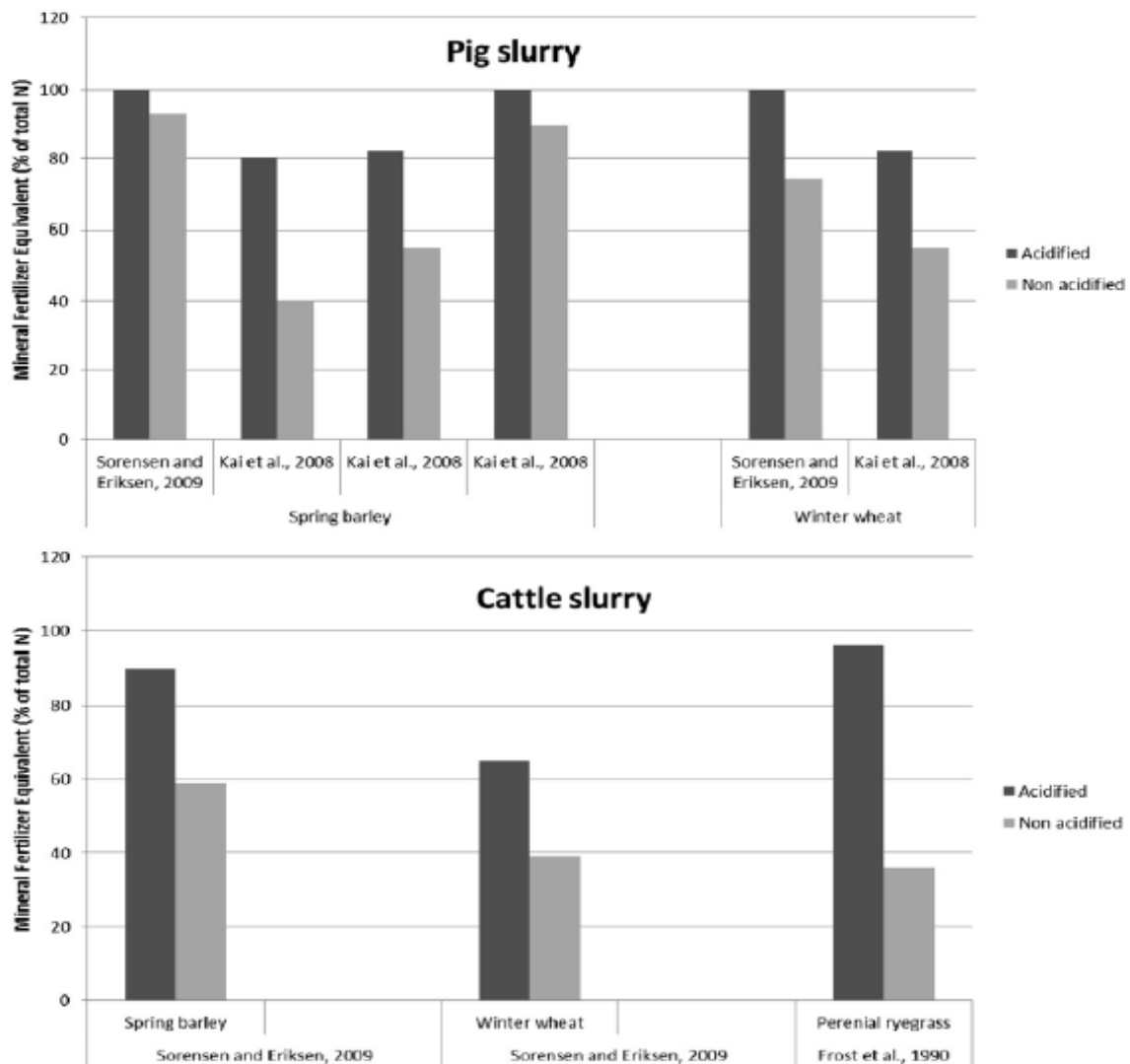
Table showing overall impact of acidification on the gases, NH₃, N₂O, CO₂, H₂S and CH₄ and at which stage of the manure management process it was investigated. (Fangueiro et al. 2015).

Ammonia (NH₃)

As with most technologies related to ammonia reduction, the effectiveness of ammonia reduction depends on various parameters. Fangueiro et al. (2015) suggested these are the additive used, target pH, slurry type and the stage in the slurry management chain where additive is applied. The most efficient acidifiers are strong acids such as sulphuric acid (H₂SO₄), hydrochloric acid (HCl) or nitric acid. Lactic acid reduced NH₃ emissions by 65 - 88%, with pH values between 5.7 and 4.2, whereas nitric acid reduced NH₃ emissions by only 29 - 71% for the same pH values. Following field application acidification, decreases of NH₃ emissions in the range of 40 - 80% with pig slurry and 15 - 80% with cattle slurry depending on slurry dry matter and weather parameters.

Nitrous Oxide (N₂O)

Fangueiro et al. (2010) investigated the N₂O emissions from a sandy soil amended with acidified or non-acidified pig slurry and then with the liquid and solid fractions obtained after separation of the acidified slurry. Over the first 47 days lower N₂O emissions were observed from the acidified slurry and the liquid and solid fractions. But later, higher emissions were observed from acidified raw slurry, whereas emissions from the acidified liquid and solid fractions remained lower than from the non-acidified liquid and solid fractions, respectively. The authors reported that acidification can delay nitrification and consequently denitrification, the main source of N₂O.



Effect of slurry acidification on mineral fertiliser equivalent for pig and cattle slurries. Fangueiro et al (2015)

The reductions in ammonia emissions serve to increase the fertiliser value of slurries as shown in the graph above.

Effects of acidification

Carbon dioxide (CO₂)

Following soil application, lower CO₂ emissions were observed in soil amended with acidified pig or cattle slurry relative to non-acidified slurries. Decreased CO₂ emissions can reflect lower microbial activity in the soil, a negative impact on nutrients cycling but increasing the amount of carbon stored in the soil (Fangueiro et al., 2015).

Methane (CH₄)

Slurry acidification acts on methanogenesis; therefore, CH₄ emissions should be lowered by long-term acidification treatments, but not by short-term acidification. The reason may be an increased number of protonated acids, which act as an inhibitor (Fangueiro et al., 2015). Published studies targeting different pHs reported decreases >90% with lactic acid against 67 -

87% with sulphuric acid, 40 - 65% with Hydrochloric acid, and 17 - 75% with nitric acid (Fangueiro et al., 2015).

Hydrogen Sulphide (H₂S)

Literature is divided on whether acidification decreases or has no impact hydrogen sulphide production with studies showing both (Fangueiro et al., 2015). Increases in H₂S have been observed immediately after acidification but this can happen because existing sulphide is protonated and because of the initiation of mixing which will happen in most situations (Fangueiro et al., 2015).

Acidification using sulphuric acid may increase H₂S production by increasing the activity of sulphate reducing bacteria can be stimulated by the addition of inorganic sulphur (Dai and Blanes-Vidal, 2013). However, the bacteria are also sensitive to pH and consequently, acidification to low pH may limit their activity and H₂S emissions (Eriksen et al., 2008). Additionally, H₂S emissions can be avoided by oxygenation of acidified slurry (Jensen, 2002). Furthermore, the lower rate of organic matter degradation including protein may decrease the production of sulphate and thus sulphide.

References

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