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REPORT

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An Online-Monitoring and Operating System to Prevent Odour and Corrosion in Sewer Networks

Feasibility Study

Project Acronym: ODOCO-1

by

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Abstract

Project name: **An Online-Monitoring and Operating System to prevent Odour and Corrosion in Sewer Networks**
Phase 1: Feasibility Study “ODOCO-1”

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Odours emerging from sewage networks are unpleasant, can cause health impacts on sewer workers and impair public perception of the operator companies. Corrosion is one of the causes for the cost of repairs for damages to wastewater systems in the public sewage network, which are rising extremely [DWA, 2004]. Both phenomena can have their origin in biogenic acid corrosion that is illustrated in this report. The Kompetenzzentrum Wasser Berlin (KWB) commissioned the Technical University Berlin and the Material Testing Institute of Berlin-Brandenburg to give a report on:

- State of the art on control systems for odours and corrosion problems in sewer networks,
- State of the art on sensor technologies for water, gas and corrosion parameters to follow corrosion and H_2S production,
- Investigation on the feasibility to develop a three-phase model to predict the mass transfer of H_2S from water to the gas phase and to the wall of the pipe through the biofilm and
- Elaboration of a draft of the functional and technical specifications for a sewer network pilot plant.

Control systems

The report contains recently acquired knowledge about processes and process parameters that lead to odour and corrosion. Biochemical and physical mechanisms as well as their enhancing and hindering frame conditions are explained in detail. Literature study

and own investigations show that retention time, temperature and biological activity are relevant in all parts of the system, that is liquid and gaseous phase as well as biofilm below and above water level. Furthermore, redox potential, pH-value and ratio of submerged biofilm to wastewater volume are important quantities in sewage and biofilms. Type of sewage network, type of pumping and constructive features demonstrate an influence on production of odour and corrosion, too. Attempts were made to quantify the influence of these parameters. But for all those efforts, neither the critical point of retention time could be determined nor correlation with temperature is generally quantified. Not even the inclusion of a number of relevant parameters in empirical equations (COD, sulphur content etc.) of various authors (THISTLETHWAYTE, BOON & LISTER, ATV, US EPA, POMEROY, HVITVED-JACOBSEN) result in satisfying predictions. Practical criteria for example keeping in a certain H_2S-conentration or retention time are not available. So detailed investigations should be carried out, to get more knowledge about the processes and their influencing parameters.

Odours and corrosion can be controlled with various countermeasures. Countermeasures that are often used and approved as well as new approaches will be explained. They utilise methods of enrichment with oxidants, precipitation of sulphide, pH-regulation, gas treatment with biofilters, covering systems and constructive solutions. Feedback control systems permit to ensure the right choice and adjustment of countermeasures. Data on the state of material, online-measured parameters and experienced patterns trigger the adequate adjustment. Several examples are given for this relatively new field. It can be concluded, that deeper knowledge about relationships between parameters and odour or corrosion, including knowledge about kinetics of these processes, would be helpful to adjust countermeasures automatically. Optimized dosage concepts can achieve economical application of those chemical methods. A reliable prediction technique based on modeling, could support this.

Measurements

The investigation on existing sensors in relation to the necessary parameters to be measured, determining the condition of technical wastewater facilities, regarding the presence of odour and corrosion effective substances, results in the following:

Plastic corrosion (aromatic and halogenated hydrocarbons)

Sensory processes for the continuous monitoring of concentration of halogenated and aromatic hydrocarbons in sewage do not exist. For detection in the headspace, the IR-sensor shows the highest selectivity (detection of CH-binding) and is suitable for environments of very high humidity.

Concrete corrosion (sulphuric acid)

There are no proven methods for continuous sensory determination of pH-values and concentration of sulphate in biofilm. In particular, the development of sensors for continuous monitoring of pH-values in biofilm of the headspace would be highly relevant for the early detection of possible damage in wastewater facilities through dissolving concrete corrosion.

There is a functioning prototype of a fibre optic sensor for the sensory detection of pH-value in reinforced concrete of wastewater facilities currently in development with the participation of the MPA Berlin-Brandenburg. The system is within the scope of a further research project, currently being tested.

Odour (H_2S)

For the H_2S-measurement in the headspace, different measurement principles are established. It cannot definitely be established, to which extent the sensors can deliver sufficiently stable measuring signals for the long-term continuous measurement of H_2S in the headspace of wastewater facilities.

Additional parameters for modelling

For the determination of additional parameters that are important for the acquisition and modelling of chemical and biological relationships only sensors for continuous determination of oxygen concentration in the wastewater are used in the practice. For the continuous determination of sulphide-content in wastewater, the existing sensors show low long-time stabilities and high-cross sensitivities. Here are just analysers available that take virtually continual probes from the wastewater stream and carry out automated analysis. For all other parameters (e.g. organic sulphur compounds, COD, BOD in wastewater), there are also only laboratory procedures or expensive virtually continual procedures where sewage is extracted and analyzed in accordance to laboratory procedures.

The organic load, determined by COD and BOD can be correlated to UV-absorption to some extent. But anyhow, they need calibration against COD and BOD of a specific sewage. The practicability of applying UV-probes should be tested in the further experiments.

The procedures for determining biological activity of biofilms are in the development stage. It is not clear whether the measurement of biofilm activity is sufficiently specific enough to deliver relevant information on the problems of odour and corrosion. On the other hand, the measurement of physical parameters (relative humidity, temperature, air pressure and flow rate), is well established.

Data processing

The necessity to implement an integrated data processing and storage system is strongly recommended. Large data sets, documenting sensorially and analytically won measurements, are emerging in the process of monitoring sewage systems for control of odour and corrosion. Units of data have to be reasonably and automatically captured and pre-processed. They form the basis for any calibration and validation of the numerical models, as well as the foundation to assess the model-quality. Since a comprehensive study investigating the field of data processing was not targeted, only a short depiction of the required tasks and the potential approaches are given.

Modelling

Empirical formulas are just capable of giving a very rough estimation of the sulphide development in sewers and they are poorly transferable to general conditions. Urban drainage, wastewater plant and water quality models have some more or less close relations to the simulation of flow, transport and reactions processes in sewers systems. Among, the very few models which are capable to simulate the above-mentioned processes, only the WATS model has been applied to odour and corrosion problems in sewer systems.

The WATS model has its strength in simulating the microbial and chemical reaction processes of organic matter, sulphur and other components in the water and gas phase including mass transfer water-gas and corrosion with a focus on dry weather conditions. Current deficits of WATS are in the flow simulation (no non-uniform and instationary water flow, no turbulence, no gas flow) and the transport simulation (no diffusion / dispersion in water and gas, no sediments and erosion / deposition). Problems dealing for example with rainwater conditions, ventilation, flushing, flow over drops can not be treated with WATS. Furthermore, the numerics and the software design can be improved. The WATS model is not public domain, and the sources and the software are not available. However, the developers are very open for collaborations (personal communication). The amount of the source code is not very high and all methods are published. The quality of the WATS model strongly relies on the availability and quality of data, and many data of the WATS group are published, too.

In future work, a three-phase model will be developed including the phases water, gas and solid (sewer wall) for prediction odour and corrosion in sewer systems. The model will solve the coupled equations for flow, transport and reaction in the water and gas phase including mass-transfer processes (hydrogen sulphide, oxygen). Based on previous work, it will use the Finite-Volume Method and it will be embedded in an object-orientated framework. The major focus of the model will consist of biological and chemical transformations of carbon, sulphur, and nitrogen. First, a calibration and validation in a pilot sewer under controlled conditions is required. In further steps, it can applied for designing countermeasures (ventilation, dosages, flushing, ...) and it can be transferred to real sewer systems. The three-phase model will be part of a closely linked monitoring and prediction system.

Outlook

The results of the feasibility study (ODOCO-1) show that it is possible to develop a prediction technology. Further studies shall be carried out at a sewer pilot plant where conditions can be controlled and parameters of odour and corrosion are adjustable. Existing sensor technologies will be applied and improved for capturing of correlations. After data processing and storage, this information is available for investigation on biochemical and transport processes. A three-phase model will be built on the base of this information. With the help of this model, countermeasures can be adjusted accurately in a feedback control system. A detailed draft of a sewer pilot plant is given in the proposal for “Developing a prediction technology using studies at a pilot plant ODOCO-2” in the appendix.

Zusammenfassung

Projektname: **Online-Überwachungs- und Betriebssystem zur Geruchs- und Korrosionsverhinderung in Kanalisationsnetzen**
Phase 1: Machbarkeitsstudie “ODOCO-1”

Dauer: **4/2007 bis 12/2007**

Volumen: **48.750 Euro**

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Aus Kanalisationsnetzen aufsteigende Gerüche sind unangenehm, sie können Gesundheitsprobleme bei Kanalarbeitern hervorrufen und den Ruf der Betreiberfirmen schädigen. Korrosion ist eine der Ursachen für die stark steigenden Kosten, die bei der Beseitigung von Schäden an Abwassersystemen in öffentlichen Kanalisationsnetzen anfallen [DWA, 2004]. Beide Erscheinungen können durch die in diesem Bericht betrachtete biogene Säurekorrosion verursacht sein. Das Kompetenzzentrum Wasser Berlin (KWB) beauftragte die Technische Universität Berlin und das Materialprüfungsamt Berlin-Brandenburg mit einem Bericht über:

- den Stand der Technik bei Kontrollsystemen für Geruchs- und Korrosionsprobleme in Kanalisationsnetzen,
- den Stand der Technik bei Sensortechnologien für Wasser-, Gas- und Korrosionsparameter zur Beobachtung der Korrosion und der H_2S-Erzeugung,
- die Untersuchung der Machbarkeit eines Dreiphasenmodells zur Vorhersage des Stoffübergangs von H_2S aus dem Wasser in die Gasphase und in die Rohrwand durch den Biofilm und
- die Erarbeitung eines Entwurfs der funktionalen und technischen Spezifikationen für eine Pilotanlage im Kanalisationsnetz.

Kontrollsysteme

Der Bericht enthält neue Erkenntnisse über Prozesse und Prozessparameter, die Geruch und Korrosion hervorrufen. Biochemische und physikalische Mechanismen sowie ihre förderlichen und hinderlichen Rahmenbedingungen werden im Detail erklärt. Ein Literaturstudium und eigene Untersuchungen der Autoren zeigen, dass Retentionszeit, Temperatur und biologische Aktivität in allen Teilen des Systems relevant sind, also in der flüssigen und der Gasphase ebenso wie in dem Biofilm über und unter dem Wasserspiegel. Außerdem sind das Redoxpotential, der pH-Wert und das Verhältnis zwischen dem Biofilm unter dem Wasserspiegel zum Abwasservolumen wichtige Größen im Abwasser und in Biofilmen. Effekte von Geruch und Korrosion werden auch durch die Art des Kanalisationsnetzes und der Pumpeinrichtungen sowie die Bauweise beeinflusst. Es wurde bereits vielfach versucht, den Einfluss dieser Parameter zu quantifizieren. Bei all diesen Bemühungen konnte aber weder der kritische Punkt der Retentionszeit bestimmt werden, noch wurde die Korrelation mit der Temperatur überhaupt quantifiziert. Selbst die Berücksichtigung einiger relevanter Parameter in empirischen Gleichungen (CSB, Schwefelgehalt usw.) verschiedener Autoren (THISTLETHWAYTE, BOON & LISTER, ATV, US EPA, POMEROY, HVITVED-JACOBSEN) führte nicht zu befriedigenden Ergebnissen. Beispielsweise sind keine praktischen Kriterien für die Einhaltung einer bestimmten H_2S-Konzentration oder Retentionszeit verfügbar. Es sollten also eingehendere Untersuchungen durchgeführt werden, um mehr Wissen über die Prozesse und die sie beeinflussenden Parameter zu erhalten.

Gerüche und Korrosion können mit verschiedenen Gegenmaßnahmen kontrolliert werden. Es werden oft angewendete und erprobte Gegenmaßnahmen und auch neue Verfahren erläutert. Sie nutzen Methoden der Anreicherung mit Oxidantien, die Sulfidausfällung, die pH-Einstellung, die Gasbehandlung mit Biofiltern, Abdecksysteme und bauliche Lösungen. Rückkopplungsregelungssysteme geben die Möglichkeit, die richtige Auswahl und Anpassung der Gegenmaßnahmen zu gewährleisten. Daten über den Materialzustand, online gemessene Parameter und erfahrungsgemäße Muster dienen der adäquaten Anpassung. Für dieses verhältnismäßig neue Gebiet werden mehrere Beispiele gegeben. Man kann daraus schließen, dass vertieftes Wissen über Beziehungen zwischen Parametern und Geruch und Korrosion, einschließlich von Wissen über die Kinetik dieser Prozesse, hilfreich bei einer automatischen Anpassung der Gegenmaßnahmen wäre. Optimierte Dosierungskonzepte können für die wirtschaftliche Anwendung dieser chemischen Verfahren sorgen. Ein auf Modellierung beruhendes zuverlässiges Vorhersageverfahren könnte das unterstützen.

Messungen

Die Untersuchung vorhandener Sensoren in Bezug auf die zu messenden Parameter für die Bestimmung des Zustands technischer Abwasseranlagen unter Berücksichtigung der Anwesenheit geruchs- und korrosionswirksamer Stoffe kam zu den folgenden Ergebnissen:

Kunststoffkorrosion (aromatische und halogenierte Kohlenwasserstoffe)

Sensorverfahren zur kontinuierlichen Überwachung der Konzentration halogenierter und aromatischer Kohlenwasserstoffe im Abwasser gibt es nicht. Bei der Messung im Kopfraum zeigt der IR-Sensor die höchste Selektivität (Anzeige der CH-Bindung). Er ist für Umgebungen mit sehr hoher Feuchtigkeit geeignet.

Betonkorrosion (Schwefelsäure)

Es gibt keine erprobten Methoden für die kontinuierliche Sensormessung von pH-Werten und Sulfitkonzentration im Biofilm. Insbesondere die Entwicklung von Sensoren zur kontinuierlichen Messung von pH-Werten im Biofilm des Kopfraums wäre sehr relevant für den frühen Nachweis möglicher Schäden an Abwasseranlagen durch Beton zerstörende Korrosion.

Es gibt einen funktionierenden Prototyp eines Glasfasersensors zur Bestimmung des pH-Werts in bewehrtem Beton von Abwasseranlagen, der zur Zeit in Zusammenarbeit mit der MPA Berlin-Brandenburg entwickelt wird. Das System wird gegenwärtig im Rahmen eines Forschungsprojekts geprüft.

Geruch (H_2S)

Für die H_2S-Messung im Kopfraum gibt es verschiedene Messverfahren. Es kann nicht mit Sicherheit festgestellt werden, in welchem Maße die Sensoren hinreichend stabile Messsignale bei der kontinuierlichen Langzeitmessung von H_2S im Kopfraum von Abwasseranlagen liefern können.

Weitere Modellierungsparameter

Im Hinblick auf die Bestimmung weiterer Parameter, die für die Ermittlung und Modellierung chemischer und biologischer Beziehungen von Bedeutung sind, werden in der Praxis nur Sensoren zur Bestimmung der Sauerstoffkonzentration im Abwasser genutzt. Bei der kontinuierlichen Bestimmung der Sulfidkonzentration im Abwasser weisen die vorhandenen Sensoren niedrige Langzeitstabilitäten und hohe Querempfindlichkeiten auf. Hier gibt es nur Messgeräte, die virtuell kontinuierliche Proben aus dem Abwasserstrom entnehmen und eine automatisierte Analyse vornehmen. Auch bei allen anderen Parametern (z. B. organische Schwefelverbindungen, CBS, BDS im Abwasser) gibt es nur Laborverfahren oder teure virtuell kontinuierliche Verfahren, bei denen Abwasser extrahiert und mit Hilfe von Laboratoriumsverfahren analysiert wird.

Die durch CSB und BSB bestimmte organische Belastung kann in gewissem Maße mit der UV-Absorption korreliert werden. Irgendwie müssen diese Messungen aber durch Beziehen auf CSB und BSB eines bestimmten Abwassers geeicht werden. Die Praktikabilität der Verwendung von UV-Sonden sollte in weiteren Experimenten geprüft werden.

Die Verfahren zur Bestimmung der biologischen Aktivität von Biofilmen sind noch im Entwicklungsstadium. Es ist unklar, ob die Messung der Biofilmaktivität spezifisch genug ist, um relevante Informationen zu den Problemen von Geruch und Korrosion zu liefern. Andererseits ist die Messung physikalischer Parameter (relative Feuchtigkeit, Temperatur, Luftdruck und Durchsatz) durchaus bewährt.

Datenverarbeitung

Die Anwendung eines integrierten Datenverarbeitungs- und Speichersystems ist dringend zu empfehlen. Bei der Überwachung von Abwassersystemen zur Kontrolle von Geruch und Korrosion fallen große Datenmengen an, die durch Sensoren oder Analyse gewonnene Messungen dokumentieren. Die Dateneinheiten müssen in vernünftiger Weise und automatisch erfasst und vorverarbeitet werden. Sie bilden die Basis für jede Eichung und Validierung der numerischen Modelle und sind die Grundlage für die Bewertung der Modellqualität. Da eine umfassende Untersuchung in Bezug auf das Gebiet der Datenverarbeitung nicht beabsichtigt war, wird nur eine kurze Beschreibung der erforderlichen Aufgaben und der potentiellen Verfahren gegeben.

Modellierung

Empirische Formeln können nur eine sehr grobe Schätzung der Sulfidentwicklung in Abwässern liefern und sind schlecht auf allgemeine Bedingungen übertragbar. Stadtentwässerungs-, Klärwerks- und Wasserqualitätsmodelle haben einige mehr oder weniger enge Beziehungen zur Simulation von Strömungs-, Transport- und Reaktionsprozessen in Kanalisationssystemen. Von den sehr wenigen Modellen, die die oben genannten Prozesse simulieren können, ist nur das WATS-Modell auf Geruchs- und Korrosionsprobleme in Abwassersystemen angewendet worden.

Die Stärke des WATS-Modells liegt in der Simulierung der mikrobiellen und chemischen Reaktionsprozesse von organischer Substanz, Schwefel und anderen Bestandteilen in der wässrigen und der Gasphase, einschließlich des Stoffaustauschs Wasser-Gas und der Korrosion, mit einem Schwerpunkt auf den Bedingungen bei trockenem Wetter. Die derzeitigen Defizite des WATS-Modells liegen in der Strömungssimulation (keine ungleichmäßige und instationäre Wasserströmung, keine Turbulenz, kein Gasstrom) und der Transportsimulation (keine Diffusion/Dispersion in Wasser/Gas, keine Sedimente und Erosion/Ablagerung). Beispielsweise können Probleme, die mit Regenwasserbedingungen, Belüftung, Spülung oder Überläufen verbunden sind, nicht mit WATS behandelt werden. Außerdem sind die Numerik und die Software-Gestaltung verbesserungsfähig. Das WATS-Modell ist nicht lizenzfrei, und die Quellen und die Software sind nicht verfügbar. Die Entwickler sind jedoch sehr offen für Zusammenarbeit (persönliche Mitteilung). Der Umfang des Quellcodes ist nicht sehr groß und alle Methoden sind veröffentlicht. Die Qualität des WATS-Modells hängt stark von Verfügbarkeit und Qualität der Daten ab, viele Daten der WATS-Gruppe sind auch veröffentlicht.

In der zukünftigen Arbeit wird ein Dreiphasenmodell zur Vorhersage von Geruch und Korrosion in Kanalisationssystemen entwickelt werden, das die Phasen Wasser, Gas und Feststoff (Kanalwand) einbezieht. Das Modell wird die gekoppelten Gleichungen für Strömung, Transport und Reaktion im Wasser und in der Gasphase lösen, einschließlich der Stoffaustauschprozesse (Schwefelwasserstoff, Sauerstoff). Auf früheren Arbeiten beruhend wird die Methode finiter Elemente angewendet. Der Schwerpunkt des Modells wird die Abbildung von biologischen und chemischen Transformationen von Kohlenstoff, Schwefel und Stickstoff bilden. Zuerst sind eine Eichung und die Validierung in einer Pilotkanalisation unter kontrollierten Bedingungen erforderlich. In weiteren Stufen kann das Modell für das Entwerfen von Gegenmaßnahmen (Belüftung, Dosierungen, Spülen usw.) eingesetzt werden, und es kann dann auf reale Kanalisationssysteme angewendet werden. Das Dreiphasenmodell wird Bestandteil eines eng vernetzten Überwachungs- und Vorhersagesystems sein.

Ausblick

Die Ergebnisse der Machbarkeitsstudie (ODOCO-1) zeigen, dass es möglich ist, eine Vorhersagetechnologie zu entwickeln. Weitere Untersuchungen sollten an einer Abwasserpilotanlage durchgeführt werden, in der die Bedingungen kontrolliert werden können und die Parameter von Geruch und Korrosion anpassbar sind. Hier können vorhandene Sensortechnologien angewendet und verbessert werden, um Korrelationen zu erfassen. Nach Datenverarbeitung und Speicherung stehen diese Informationen für Untersuchungen von biochemischen und Transportvorgängen zur Verfügung. Beruhend auf diesen Informationen könnte ein Dreiphasenmodell erstellt werden. Mit Hilfe dieses Modells können Gegenmaßnahmen in einem regelungstechnischen System genau angepasst werden. Im Anhang ist ein detaillierter Entwurf einer Abwasserkanalpilotanlage enthalten mit einem Vorschlag zur “Entwicklung einer Vorhersagetechnologie auf Grund von Untersuchungen an einer Pilotanlage ODOCO-2“.

Résumé

Nom de projet :	**Système de surveillance en ligne et d'exploitation en vue de prévenir l'apparition d'odeurs et de corrosion dans les réseaux d'assainissement** **Phase 1: Étude de faisabilité « ODOCO-1 »**
Durée :	**04/2007 à 12/2007**
Volume :	**48.750 euros**
Réalisation :	**Prof. Dr. Matthias Barjenbruch**, Université Technique de Berlin, Institut de génie civil, Discipline: Gestion des eaux urbaines, Chaire de fondation KWB – Veolia Wasser **Dr. Bodo Weigert**, KWB **Christophe Renner**, Anjou Recherche
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Les odeurs en provenance des réseaux d'assainissement sont désagréables, elles peuvent provoquer des problèmes de santé chez les égoutiers et porter atteinte à la réputation des entreprises exploitantes. La corrosion est une des causes de la forte augmentation des coûts survenant lors de l'élimination de dommages au niveau des systèmes d'évacuation des eaux usées dans les réseaux d'assainissement publics [DWA, 2004]. Ces deux phénomènes peuvent être causés par la corrosion par acide biogène faisant l'objet de ce rapport. Le Centre de Compétence des Eaux de Berlin (KWB) a demandé à l'Université Technique de Berlin et l'Office d'examen des matériaux de Berlin-Brandebourg un rapport sur :

- L'état actuel de la technique en matière de systèmes de contrôle pour les problèmes d'odeurs et de corrosion dans les réseaux d'assainissement,
- L'état actuel de la technique en matière de technologies de capteurs pour les paramètres d'eau, de gaz et de corrosion en vue de l'observation de la corrosion et de l'apparition de H_2S,
- L'analyse de faisabilité d'un modèle à trois phases en vue de prévoir le transfert de matière de H_2S de l'eau à la phase gazeuse et dans la paroi des tubes à travers le biofilm, et
- L'établissement d'une ébauche des spécifications fonctionnelles et techniques pour une installation pilote dans le réseau d'assainissement.

Systèmes de contrôle

Le rapport contient de nouvelles connaissances sur les processus et les paramètres de processus provoquant les odeurs et la corrosion. Les mécanismes biochimiques et physiques ainsi que les conditions cadres utiles et embarrassantes sont expliqués en détail. Une étude bibliographique et les analyses faites des auteurs montrent que le temps de rétention, la température et l'activité biologique dans toutes les parties du système sont intéressants, donc aussi bien dans la phase liquide et dans la phase gazeuse que dans le biofilm au-dessus et sous le niveau d'eau. En outre, le potentiel redox, la valeur de pH et le rapport entre le biofilm sous le niveau d'eau et le volume des eaux usées sont des données importantes pour les eaux usées et les biofilms. Les effets des odeurs et de la corrosion sont également influencés par le type du réseau d'assainissement et des installations de pompage ainsi que par le mode de construction. Il a déjà été tenté à plusieurs reprises de quantifier l'influence de ces paramètres. Toutes ces tentatives n'ont cependant pu aboutir ni à une détermination du point critique du temps de rétention ni à une quantification de la corrélation avec la température. Même la prise en compte de certains paramètres intéressants dans des équations empiriques (DCO, teneur en soufre etc.) de différents auteurs (THISTLETHWAYTE, BOON & LISTER, ATV, US EPA, POMEROY, HVITVED-JACOBSEN) n'a su apporter de résultats satisfaisants. On ne dispose par exemple d'aucun critère pratique pour le respect d'une certaine concentration en H_2S ou du temps de rétention. Des analyses plus approfondies doivent donc être menées afin d'obtenir plus d'informations concernant les processus et les paramètres qui les influencent.

Il est possible de contrôler les odeurs et la corrosion avec différentes contre-mesures. Le rapport explique les contre-mesures appliquées et éprouvées mais aussi de nouveaux procédés. Sont utilisées des méthodes d'enrichissement avec des oxydants, la précipitation de sulfate, le réglage du pH, le traitement de gaz avec des biofiltres, des systèmes de recouvrement et des solutions de construction. Les systèmes de réglage par rétroaction offrent la possibilité de garantir le bon choix et le bon ajustement des contre-mesures. Les données concernant l'état des matériaux, les paramètres mesurés en ligne et les modèles expérimentés permettent de réaliser un ajustement adéquat. Plusieurs exemples sont donnés pour ce domaine relativement nouveau. On peut en conclure qu'un savoir approfondi concernant les relations entre paramètres et odeurs et corrosion, incluant un savoir sur la cinétique de ces processus, serait précieux dans le cadre d'un ajustement automatique des contre-mesures. Des concepts de dosage optimisés peuvent permettre l'application rentable de ces procédés chimiques. Un procédé de prévision fiable reposant sur une modélisation pourrait servir de support.

Mesures

L’analyse des capteurs existants en regard des paramètres à mesurer pour la détermination de l’état des installations techniques d’évacuation des eaux usées, avec prise en compte de la présence de matières provoquant odeurs et corrosion, a conduit aux résultats suivants :

Corrosion des matières plastiques (hydrocarbures aromatiques et halogénisés)

Il n’existe pas de procédé de captation pour une surveillance en continu de la concentration d’hydrocarbures halogénisés et aromatiques dans les eaux usées. Lors de la mesure dans l’espace de tête, le capteur IR affiche la plus grande sélectivité (affichage de la liaison CH). Il convient aux environnements avec une humidité très forte.

Corrosion du béton (acide sulfurique)

Il n’existe pas de méthodes éprouvées pour la mesure par capteur en continu des valeurs pH et de la concentration en sulfate dans le biofilm. Le développement de capteurs pour la mesure en continu de valeurs pH dans le biofilm de l’espace de tête serait très intéressant en particulier pour la démonstration précoce de dommages éventuels au niveau d’installations d’évacuation des eaux usées par corrosion détruisant le béton.

Il existe un prototype en fonctionnement d’un capteur à fibre optique pour la détermination de la valeur pH dans du béton armé d’installations d’évacuation des eaux usées, actuellement développé en collaboration avec l’Office d’examen des matériaux de Berlin-Brandebourg. Le système est actuellement testé dans le cadre d’un projet de recherche.

Odeurs (H_2S)

Il existe différents procédés de mesure de H_2S dans l’espace de tête. Il n’est pas possible de déterminer avec certitude dans quelle mesure les capteurs sont en mesure de fournir suffisamment de signaux de mesure stables dans le cadre de la mesure longue durée en continu de H_2S dans l’espace de tête d’installations d’évacuation des eaux usées.

Autres paramètres de modélisation

En ce qui concerne la détermination d’autres paramètres importants pour l’enregistrement et la modélisation de relations chimiques et biologiques, on utilise dans la pratique des capteurs uniquement pour la détermination de la concentration d’oxygène dans les eaux usées. Dans le cadre de la détermination en continu de la concentration de sulfure dans les eaux usées, les capteurs existants présentent de faibles stabilités longue durée et des sensibilités transversales élevées. Il existe ici uniquement des appareils de mesure qui prélèvent des échantillons virtuellement continus dans le flux d'eaux usées et procèdent à une analyse automatisée. Même dans le cas des autres paramètres (p.ex. liaisons sulfuriques organiques, DCO, DBO dans les eaux usées), il n'existe que des procédés en laboratoire ou des procédés coûteux virtuellement continus pour l'extraction des eaux usées et leur analyse à l'aide de procédés de laboratoire.

La contrainte organique déterminée par la DCO et la DBO peut dans une certaine mesure être corrélée avec l'absorption de rayons UV. Ces mesures doivent toutefois être jaugées d'une manière ou d'une autre par la mise en rapport de la DCO ou de la DBO de certaines eaux usées. La praticabilité de l'emploi de sondes UV doit être testée dans des expériences à venir.

Les procédés de détermination de l'activité biologique de biofilms sont encore au stade de développement. Il n'est pas sûr que la mesure de l'activité du biofilm soit suffisamment spécifique pour fournir des informations intéressantes quant aux problèmes des odeurs et de la corrosion. D'un autre côté, la mesure de paramètres physiques (humidité relative, température, pression de l'air et débit) est tout à fait éprouvée.

Traitement des données

L'application d'un système intégré de traitement et d'enregistrement des données est vivement recommandée. La surveillance de systèmes d'évacuation des eaux usées en vue du contrôle des odeurs et de la corrosion engendre d'importantes quantités de données documentant les mesures obtenues par les capteurs ou par analyse. Les unités de données doivent être enregistrées et préparées automatiquement de manière judicieuse. Elles forment la base de tout jaugeage et de toute validation des modèles numériques et sont à l'origine de l'évaluation de la qualité des modèles. Sachant qu'il n'était pas prévu de mener une analyse globale se rapportant au secteur du traitement des données, nous ne présentons ici qu'une brève description des tâches nécessaires et des procédés potentiels.

Modélisation

Les formules empiriques ne peuvent fournir qu'une estimation très grossière de l'évolution de sulfure dans les eaux usées et sont difficilement applicables aux conditions générales. Les modèles de drainage urbain, d'usines d'épuration et de qualité de l'eau présentent quelques rapports plus ou moins étroits avec la simulation des processus d'écoulement, de transport et de réaction dans les systèmes d'assainissement. Parmi les rares modèles capables de simuler les processus mentionnés ci-dessus, seul le modèle

WATS a été appliqué aux problèmes d'odeurs et de corrosion dans les systèmes d'évacuation des eaux usées.

La force du modèle WATS repose dans la simulation des processus de réaction microbiens et chimiques de substance organique, soufre et autres composantes dans la phase aqueuse et la phase gazeuse, incluant le transfert de masse eau-gaz et la corrosion, avec une dominante au niveau des conditions par temps sec. Les déficits actuels du modèle WATS reposent dans la simulation de l'écoulement (pas d'écoulement d'eau non-homogène et non-stationnaire, pas de turbulence, pas de flux de gaz) et dans la simulation de transport (pas de diffusion/dispersion dans l'eau/le gaz, pas de sédiments ni d'érosion/dépôt). WATS ne peut par exemple pas traiter les problèmes liés aux conditions avec eau de pluie, à la ventilation, au rinçage ou aux débordements. En outre, le calcul et la conception du logiciel exigent des améliorations. Le modèle WATS fonctionne avec une licence ; les sources et le logiciel ne sont pas disponibles. Les concepteurs sont toutefois très ouverts en matière de collaboration (communication personnelle). Le volume du code source n'est pas très gros et toutes les méthodes sont publiées. La qualité du modèle WATS dépend fortement de la disponibilité et de la qualité des données et beaucoup de données du groupe WATS sont également publiées.

Le travail futur développera pour la prévision des odeurs et de la corrosion dans les systèmes d'assainissement un modèle à trois phases intégrant les phases eau, gaz et matière solide (paroi de canal). Le modèle solutionnera les équations couplées d'écoulement, de transport et de réaction dans l'eau et dans la phase gazeuse, incluant les processus de transfert de masse (sulfure d'hydrogène, oxygène). Reposant sur des travaux déjà accomplis, la méthode emploiera des volumes finis et elle sera incorporée dans un cadre tourné vers les objets. Les transformations biologiques et chimiques de carbone, de sulfure et d'azote formeront la dominante du modèle. Tout d'abord, un jaugeage et une validation dans une canalisation pilote dans des conditions contrôlées doivent être effectués. Le modèle peut être utilisé dans d'autres étapes pour l'ébauche de contre-mesures (ventilation, dosages, rinçage, …) et peut ensuite être appliqué sur des modèles de canalisations réels. Le modèle à trois phases fera partie intégrante d'un système de surveillance et de prévision étroitement mis en réseau.

Perspectives

Les résultats de l'étude de faisabilité (ODOCO-1) montrent qu'il est possible de développer une technologie de prévision. D'autres analyses doivent être menées sur une installation pilote d'évacuation des eaux usées avec possibilité de contrôler les conditions et d’adapter les paramètres d’odeurs et de corrosion. Il est possible ici d’appliquer et d’améliorer les technologies de capteurs existantes pour enregistrer des corrélations. Après le traitement des données et l’enregistrement, ces informations seront disponibles pour des analyses d’opérations biochimiques et d’opérations de transport. Un modèle à trois phases pourrait être mis en place sur la base de ces informations. À l’aide de ce modèle, des contre-mesures peuvent être ajustées précisément dans un système technique de régulation. Une ébauche détaillée d’une installation pilote de canaux pour l’évacuation des eaux usées est jointe en annexe avec une proposition de « Développement d’une technologie de prévision sur la base d’analyses menées sur une installation pilote ODOCO-2 ».

Table of Contents

Chapter 1

Introduction

The increasing centralisation of wastewater disposal has led to the extension of sewerage networks causing long detention times. A long detention time is an important precondition for wastewater to ferment. Fermenting of sewage in sewers causes several undesirable effects:

- Emergence of odour, particularly at transfer shafts from pressure into gravity systems
- Corrosion of sulphuric acid in pipelines, shafts, and special structures
- Health impacts on sewer workers
- Possibly negative effects on the wastewater purification

Especially the emergence of odour increasingly causes acceptance problems for the wastewater disposal companies. For this reason, the amount of chemicals used for septicity prevention has risen immensely [YANG & HOBSON, 2001]. In most cases, corrosion leads to considerable costs in the long run. E.g. Veolia Eau Germany employs 800 t/a Nutriox ® for about 200 000 €/a.

First, problems of odour and corrosion will be illustrated. In the second section, causing processes are presented. Chapter 3 and Chapter 4 present sensor technologies to detect all necessary parameters and show how to process and store the resulting data. The state of the art on countermeasures and control systems for odour and corrosion problems in sewer networks is described in Chapter 5. Existing model concepts are introduced and their potentials for prediction of odour and corrosion are assessed in Chapter 7. Based on the knowledge of causing processes and effects of countermeasures, approved and possible feedback control systems are presented in Chapter 6. A preproposal for further investigation on “An Online-Monitoring and Operating System to prevent Odour and Corrosion in Sewer Networks – Pilot Plant and Prediction Model” has been elaborated by the authors and is a supplement to this report.

1.1 Odour

Odour is “the property of a substance that is perceptible by the sense of smell” [OXFORD ENGLISH DICTIONARY]. “The perception of odour occurs when an odourant (the smell) enters the nasal cavity and excite the osmoreceptors ... Certain parts of an odourous molecule are responsible for the characteristic smell. These are called osmogenes. The sulphuryl group (S–H) is one such osmogene" [ENVIRONMENT AGENCY UK, 2001].

Raw sewage from households has a characteristic musty smell, resulting from its components. Although it is not pleasant, it rarely gives rise to odour problems [HORAN & MARA, 2003], if there are no industrial discharges that contain primary osmogenes.

Secondary osmogenes need time to develop. Therefore, they emerge from aged sewage in wastewater treatment systems. Common sewage odour compounds are sulphides (hydrogen sulphide, methylmercaptan, ethylmercaptan, (di)methyl(di)sulphide), nitrogen containing compounds (ammonia, (di)methylamine, indole, skatole), acids (acetic, butyric, valeric), aldehydes (formaldehyde) and ketones. The amount of a compound released to the atmosphere depends on various parameters. E.g., the pH-value determines the chemical state of a compound in the liquid phase. Low pH-values favour the emission of H_2S, mercaptans and volatile fatty acids, while high pH-values favour the emission of ammonia and amines. In general, odours at high pH-values are less intense, causing rarely odour nuisance. Therefore, it is justified to focus on odours emerging from neutral to acid wastewater [HORAN & MARA, 2003]. In this range of pH-value, hydrogen sulphide is acknowledged as a keynote parameter for odour nuisance from household sewage. As H_2S is the dominant odorant here, concentration of H_2S in gas phase is an acceptable surrogate for odour [FRECHEN, 2007]. The buildup of hydrogen sulphide is described below in sec. 2.1.1.

1.2 Corrosion

The term "corrosion" describes all reactions on metallic and non-metallic construction materials with their environment, which lead through chemical, electro-chemical or microbiological processes to a detraction of the construction material. Inside sewer systems made of concrete or steel three types of corrosion are distinguished. In the submerged parts they consist of

- **Chemical corrosion**, caused directly by acid wastewaters (concrete, metals) and organic solvents (plastics)
- **Anaerobic biogenic corrosion**, where hydrogen sulphide produced by sulphate reducing bacteria attacks materials chemically, especially iron metals.

Above water level, dominating process of corrosion is the **aerobic biogenic corrosion of sulphuric acid**. Under certain conditions, this is the fastest mechanism of corrosion, so we focus on this type of corrosion [MATSCHÉ & SARACEVIC, 2007].

Corrosion ratios in dependence of the appearance of e.g. sulphates or sulphuric acids are only given for a few materials out of lab-scale experiments [BELIE et al., 2004]. Therefore, there are no forecast values to control prevention measures (see sec. 2.3 and 7.1).

Chapter 2

Causing processes

2.1 Aerobic biogenic corrosion of sulphuric acid

Hydrogen sulphide, produced below water level, strips out to the sewer atmosphere. It dissolves in condensed water of the sewer wall where it is transformed to sulphuric acid attacking the material. Sulphur species are key reactants in this process. Their transformation reactions are described below.

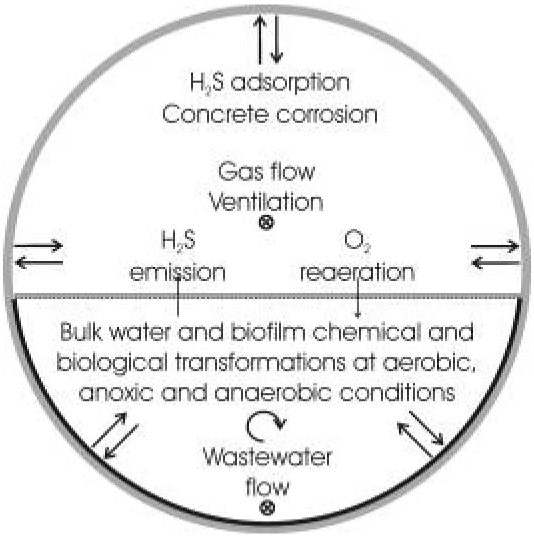


Figure 1: Microbial and chemical processes in a gravity sewer [SEWER PRO-CESSES NETWORK]

2.1.1 Formation of hydrogen sulphide (H_2S)

When sewage gets into the sewer system, bacteria from sediments, biofilms and establishing bacteria in the sewage matrix start decomposing organic carbon. As the respiration with O_2 as an electron receptor is most energy-gaining, first aerobic bacteria dominate. If the need for O_2 is not compensated by O_2-solving from the sewer atmosphere, less energy-gaining processes occur. The order of decreasing preference is oxygen, nitrate, sulphate and carbonate as electron receptors. As there are no considerable amounts of nitrate in untreated sewage, sulphate is utilised as electron receptor. Sulphate reducing bacteria (SRB) dissimilate sulphate producing hydrogen sulphide (H_2S).

They utilise products of fermenting bacteria like alcohols, organic acids and protons as reducing agent [SEWER PROCESSES AND NETWORK GROUP, 2006; MARA & HORAN, 2003]. Sulphate dissimilation takes place in anoxic parts of submerged biofilm, bulk water and sediments. HVITVED-JACOBSEN (2002) explains, that because of their slow growing rate, SRB have no chance to establish in flowing sewage, so biofilms and deposits are relevant locations of their activity. Sulphate dissimilation is the main process of H_2S-formation:

$SO_4^{2-} \rightarrow S^{2-} + HS^- + H_2S \uparrow$

Desulphuration

A less important source of sulphide is desulphuration. Fermenting bacteria hydrolyse sulphur-containing amino acids and produce H_2S [LAWA, 2004]:

$R\text{-}S \rightarrow S^{2-} + HS^- + H_2S \uparrow$

Characteristics of sulphate reducing bacteria

Distantly related bacteria are capable to reduce sulphate. They belong to genera like *desulfovibrio*, *desulfuromonas*, *desulfobulbus*, *desulfobacter*, *desulfococcus*, *desulfosarcina*, *desulfonema* and *desulfotomaculum* [POSTGATE, 1984 cited in MARA & HORAN, 2003]. Therefore, their only common feature is to dissimilate sulphate.

SRB can survive adverse conditions of temperature (5-75°C), aerobicity, salinity and pressure [MARA & HORAN, 2003].

Catabolism of SRB is strictly anaerobic although they outlive aerobic conditions. This is why development of sulphide occurs solely, if **oxygen** in the form of O_2 or NO_3^- is not available or only available in small amounts.

Redox potentials (E_h) indicate the states between aerobic and anaerobic. Current redox potential shows how active bacteria gain their energy [SEWER PROCESSES AND NETWORK GROUP, 2006]. At redox potentials within the range of -200 to -300mV they produce H_2S, resulting in a further drop in E_h [MARA & HORAN, 2003; ODOM, 1993; FUCHS, 2007]. According to BITTON (1999), SRB favour a redox potential between -150 and -200mV. HEITZ (1997) measured E_h =-375 to -250 mV on a steel surface below a biofilm of SRB compared to 50 to 150 mV without biofilm.

Anabolism of SRB is quite variable and flexible between autotrophic and heterotrophic [FUCHS, 2007]. Some varieties oxidise lactat to acetat, others oxidise it completely [MATSCHE, 2007]. On account of this, the **concentration of hydrocarbons** has no direct influence on H_2S-production. The height of concentration of **hydrocarbons** and their **biodegradability** induce the time until **dissolved oxygen** is depleted. This way it is a contributing factor to H_2S-production. For this reason, COD or ratio of COD/BOD_5 is directly related to the amount of sulphide formed [BOON, 1995; HVITVED-JACOBSEN et al., 1988 in MARA & HORAN, 2003].

Biofilms on the submerged conduits are supplied with sufficient substrate and consume about 700 mg/m²/h oxygen at 15°C [BOON & LISTER, 1975 cited in MARA & HORAN, 2003, POMEROY, 1991]. Their influence is discussed controversially. KLOSE (1981) states that the build-up of sulphide happens independently of the thickness of the submerged biofilm [LAWA. 2004]. By contrast, YANG & HOBSON (2001) show that it takes up the most oxygen. The ratio of biofilm surface to wastewater volume is higher in pipes of small diameter. Therefore, their relative rate of sulphide-formation is bigger [ATV-DVWK M 154, 2003]. This is of importance especially in rising mains with small diameters. ECKER (2003) mentions values of 700 mg $O_2/(m^2 \bullet h)$ as the maximum oxygen uptake rate in submerged biofilms [LAWA, 2004]. LOHSE (1986) found a high variability of oxygen uptake between 0,2 and 7 g $O_2/(m^2 \bullet h)$.

Beside activity of microorganisms in the submerged biofilm, **activity in the sewage** itself is important. Raw domestic sewage takes up 2 – 4 mg O_2/l/h [ECKER, 2003 IN LAWA, 2004]. During the **retention time,** bacteria populations establish and the number of microorganisms in sewage increases. Accordingly, the respiration rate and the rate of uptake of dissolved oxygen accelerate. Then, under anaerobic conditions, a growing number of microorganisms break down complex organic compounds [MARA & HORAN, 2003], producing readily biodegradable material. This is why the rate of uptake of dissolved oxygen increases with the retention time from 2 mg/l/h to 14 mg/l/h at 15°C [BOON, 1995 cited in MARA & HORAN, 2003].

LOHSE (2002) presents an empirical formula to calculate oxygen uptake rate of submerged biofilm and sewage to predict oxygen required for preventing the development of sulphide in rising mains:

$$OC = 0{,}024 \cdot \left[\pi \cdot D \cdot L \cdot \left(z_{Sh} + \frac{D \cdot z_{Abw}}{4} \right) - Q_{24} \cdot \left(c_{O2} - 1 \right) \right] \quad \left[\frac{kg}{d} \right]$$

OC = required oxygen [kg/d]
D = diameter of pipe [m]
L = length of pipe [m]
Z_{Sh} = determined oxygen uptake rate of biofilm, around 0.5 to 1.0 g O_2/m²/h at 20°C
Z_{Abw} = determined oxygen uptake rate of sewage, for 2 (respectively 20) hours aged sewage around 7 (respectively 17 g O_2/m³/h or 0.5 to 1.0 g O_2/m²/h at 20°C
Q_{24} = median of 24 h flow [m³/h]
C_{O2} = oxygen concentration at inlet of rising main [mg/l]

The influence of the **retention time** is acknowledged. LOHSE (1986 in LAWA, 2004) proves that the formation of sulphide increases up to retention times of 6 hours. BOON [1995; HVITVED-JACOBSEN et al., 1988 in MARA & HORAN, 2003] states that the **retention time** is proportional to the amount of sulphide formed. This is valuable up to a retention time of 6 hours. After 6 hours stagnation begins [LAWA, 2004]. MARA & HORAN (2003) focus especially on retaining time under anaerobic conditions as a valuable parameter. A distinct specification of a "critical age" does not make sense, because of various parameters [LAWA, 2004].

A small **flow velocity** (originating from high diameters, improper slope and low water level) contributes to a higher retention time and causes deposits that enhance anaerobicity [FRECHEN, 2007].

Temperature is a dominant parameter for concentration of H_2S in sewer atmosphere [MATSCHÉ & SARACEVIC, 2007; FRECHEN, 2007]. Its formation increases with temperature ranging from 15-27°C according to KITAGAWA in [LAWA, 2004]. Formation rate is likely to double for a 10°C increase in temperature within the range of about 5-25°C [MARA & HORAN, 2003]. The reasons for this are increased biological activity in general and on the other hand a smaller solubility of gases like oxygen and H_2S in warmer fluids, leading to a faster depletion of oxygen and a risen part of released H_2S (s. sec. 2.1.2) [BOON, 1995; HVITVED-JACOBSEN et al., 1988 in MARA & HORAN, 2003]. If temperatures exceed 25°C, increases in temperature will start to have an adverse effect on growth rate of microorganisms [MARA & HORAN, 2003]. The equation for reaction kinetics of ARRHENIUS describes effects of temperatures on microbiological activity. LOHSE (1986) cites the modified form:

$$k_T = k_{20}\,\theta^{T-20}$$

k_T = uptake rate at temperature T [1/h]
k_{20} = uptake rate at 20°C [1/h]
θ = temperature coefficient [-]
T = temperature [°C]

Temperature coefficients vary over a wide range from 1.024 to 1.139 [cited in LOHSE, 1986]. Their vast variety and dependency on temperature range and constitution of wastewater constrict application of the temperature coefficient [LOHSE, 1986].

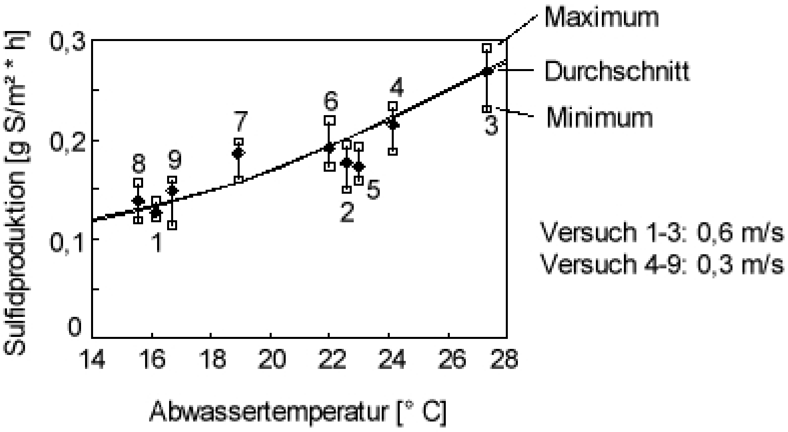


Figure 2: Production of sulphide (Sulfidproduktion) depending on wastewater temperature [KITAGAWA et al., 1998; cited in LAWA, 2004]

pH tolerance of SRB is between 5.5 and 9. An optimal condition for sulphide production is a **pH** between 6.5 [MARA & HORAN, 2003] or 7 [LAWA, 2004] and 8. Its main importance is connected to gas release [FRECHEN, 2007] (s. sec. 2.1.2).

As the largest part of H_2S production takes place in the submerged biofilm, a high ratio of **submerged surface area** to sewage volume increases specific H_2S production [LAWA, 2004; MATSCHÉ & SARACEVIC, 2007; BOON, 1995; HVITVED-JACOBSEN et al., 1988 in MARA & HORAN, 2003].

2.1.2 Transfer of hydrogen sulphide from wastewater to sewer wall

Hydrogen sulphide partly strips out of wastewater to sewer atmosphere. How much hydrogen sulphide reaches the sewer atmosphere depends on several parameters. It passes over to the air only as the gas H_2S. Therefore, **concentration of H_2S in water** is the first obvious parameter. H_2S is an acid of two protons converting to HS^- (pK_{a1}=7.04) and S^{2-} (pK_{a2}=12.9) [MATSCHÉ, 2005]. According to HVITVED-JACOBSEN (2002), the value of pK_{a2} is 14. This is why **pH** determines the part of sulphide that is available for stripping. **Alkalinity** as a characteristic of the water shows the potential range of pH [MARA & HORAN, 2003].

Mass transfer of H_2S from water phase to gas phase is liable to the general equation for mass transfer:

$$\dot{m} = A * k * (c_z - c_x)$$

$\dot{m}$ - mass flow of transferring substance [kg/h]

A - area of phase interface [m²]

k - overall mass-transfer coefficient [m/h]

c_z - equilibrium concentration [kg/m³]

c_x - concentration in gas phase [kg/m³]

Accordingly, equilibrium concentration establishes. It follows from correlation to partial pressure p_i. Equilibrium partial pressure is described in law of Henry and Dalton:

$$p_i = H_i * x_i = y_i * p_{total}$$

p - partial pressure [bar]

i - gaseous component, here H2S

H - Henry coefficient [bar]

x - portion of concentration in liquid [-]

y - portion of concentration in gas [-]

p_{total} - total pressure in system [bar]

The **Henry coefficient** depends on constituents of the system and on the temperature. For a system consisting of H_2S, air and water, the Henry coefficient has a value of 481.38 bar at 20°C (536 atm/mol at 25°C [HVITVED-JACOBSEN, 2002]). It rises with higher temperatures. Reaching of equilibrium conditions is accelerated by turbulences. The more intensive the contact between fluid and gas is the merrier is the mass transfer. It increases with turbulences, sudden falls and changes of direction. They are dominant parameters for outstripping of H_2S [FRECHEN, 2007]. When H_2S got into the sewer atmosphere, it quickly builds up a comparable equilibrium with the water phase that is condensed at the inner wall of the conduit. This place is simultanously a sink, as described in sec. 2.1.3.

If catchment areas are spacious, meteorological differences of pressure increase aeration. On the other hand, locations of odour exposure and risk of corrosion change with the meteorological situation [FRECHEN, 2007].

2.1.3 Formation of sulphuric acid (H_2SO_4)

Hydrogen sulphide, solved in condensed water, is oxidised in the biofilm of the inner surface of the conduit. Biofilms above water level have a better supply of oxygen than submerged biofilms. So **redox potential** is higher and microbiological and chemical oxidation processes occur [SEWER PROCESSES AND NETWORK GROUP, 2006]. The range of redox potentials of chemolitotrophic microorganisms using H_2S as electron donor and O_2

as electron receptor is between -0.22 and +0.8V [FUCHS, 2007]. Sulphide and its chemical oxidation products are oxidised by bacteria like *Thiobacilli* to sulphuric acid, which reacts with concrete to form gypsum [SAND & BOCK, 1984 cited in ODOM, 1993]. As the water at the surface of the conduit is condensed water, it does not provide sufficient **alkalinity** to prevent low pH-values. Therefore, pH drops without barriers. The optimal **pH** for sulphuricating bacteria is 1-3 [FUCHS, 2007].

Sulphuricating bacteria are mostly fastidious lithotrophic, using H_2S or other not-oxidised sulphur-compounds as electron donators. Their anabolism is **autotrophic**, sometimes facultative [FUCHS, 2007], which means that they build up their cells with carbon out of CO_2.

$$H_2S + O_2 \rightarrow 2\ H_2O + 2\ S$$
$$S^{2-} + 2\ O_2 \rightarrow 2\ SO_4^{2-}$$
$$S + H_2O + 1.5\ O_2 \rightarrow H_2SO_4$$

In addition, H_2SO_4-production accelerates with the rise of **temperature** [ODOM, 1993]. The optimal temperature is about 30°C [FUCHS, 2007].

Table 1: Summary of factors that influence the production of sulphide

Factors	Effects
Sulphate contents	development of sulphide increases with increasing sulphate contents (Monod); inhibition < 30 mg/l [LOHSE, 2002]
Temperature	development of sulphide increases with rising temperatures
Organic pollution	different results: partly no influence, partly increasing
Redox potential	production of sulphide only if wastewater is in anaerobic conditions (< 0,1 mg O_2/l)
Biofilm	consumes the most oxygen
pH-value	tolerant in width range of pH; between 5,5 to 9,0
Flow velocity	generally no considerable influence; a thicker biofilm is produced in case of lower flow velocities
Flow time	in case of long detention periods, wastewater changes into anaerobic state; critical detention period difficult (appr. > 2 to 4 hours)
Operation method	with pumps operating continuously and with flow times of up to 6 hrs, values are 10-20 % higher than they would be with discontinuous operation [LOHSE, 2002]

2.2 Typical locations in which odour and corrosion occur

There are locations in sewer networks likely to suffer odour and corrosion. These are points where odour-enhancing conditions (described in sec. 2.1.1) coincide. Conditions of long detention times, depletion of oxygen and turbulences occur, for instance, after rising mains in transferring shafts, pumping stations, ramp manholes and turn-off shafts. Depending on the construction (separate or combined system, special dewatering methods), the critical osmogenes can develop at different locations in the sewage system and under different frame conditions (Table 2). It is often experienced that maximum H2S-concentrations are measured behind points of critical conditions. Generally, it should be paid attention to the fact that anaerobic wastewater is to be transported as carefully as possible to avoid any gas emission.

Table 2: Problematic locations where odour hazards may occur in the sewage system

Problematic location	Causes	Problems
Gravity sewers	anaerobic state (long detention time; low slope, low v_F) (e.g. during dry weather in a combined sewerage system)	depends on construction and operation
Ramp manhole	depends on the incoming wastewater: anaerobic → odour aerobic → odour low	Stripping out of previously formed osmogenes and possibly odour harassment
Turn-off shaft	change of direction or slope	see above
Wastewater pump stations	long contact times in the collecting container; filling of the collection container above the minimum water level	Creation of an anaerobic milieu Stripping out of osmogenes
Transferring shaft of rising mains	Wastewater from pressure pipeline has possibly begun to ferment in long flow times	Osmogenes are stripped out
Industrial discharge	wastewater loaded with osmogenes wastewater with high temperatures	Indirect discharger control

In view of the fact that frame conditions change in many places (only partly developed settlement and industrial areas, decreased specific wastewater production), the **transferring shafts of rising mains** with long retention times are particularly problematic, because osmogenes can be emitted from the wastewater with an anaerobic milieu into the surrounding air. In the long term, it must be expected that corrosion problems will arise as well (Figure 3).

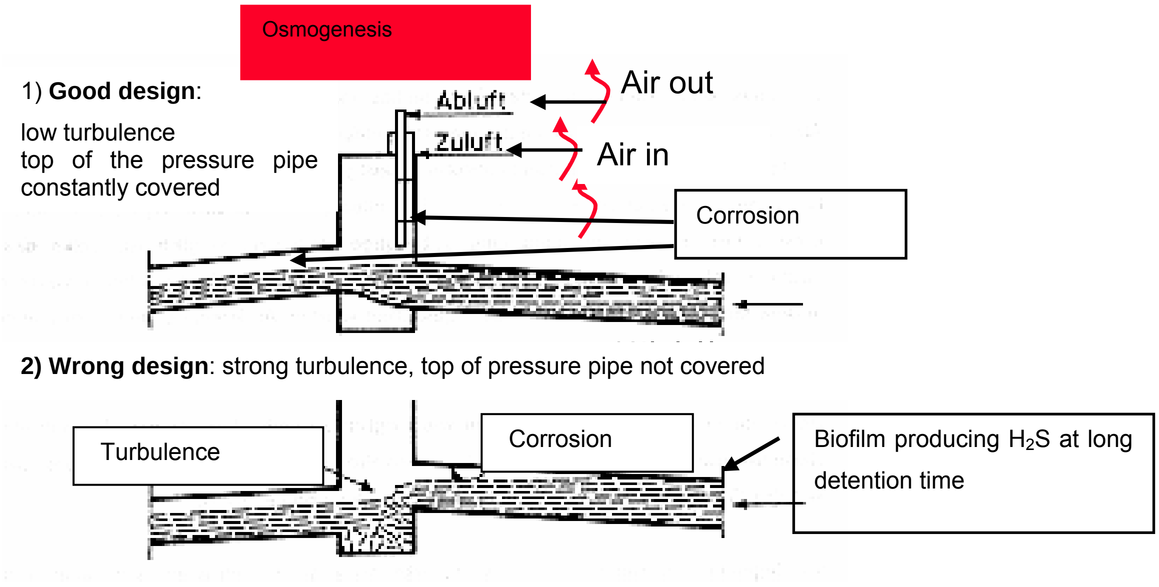


Figure 3: Odour development and corrosion at the transferring shaft [KLOSE, 1981] modified

2.3 Concrete corrosion by H_2SO_4

2.3.1 Introduction

According to the latest survey report 2004 by the German Water Management, Wastewater and Refuse Association (Deutsche Vereinigung für Wasserwirtschaft, Abwasser und Abfall e.V., DWA) the cost of repairs for damages to wastewater systems in the public sewage network will amount to approx. 55 billion Euros in Germany. It is estimated that the same amount will have to be invested in the short and medium term for the repair of sewage systems in the private sector (private households, industry).

One of the causes for this is the corrosion of construction material by chemically corrosive substances. The most significant harmful substance for concrete as a construction material in sewage systems is sulphuric acid.

2.3.2 Biogenic acid corrosion

Concrete is severely damaged by acids. As the aggregates in concrete are normally virtually acid-insoluble, the acids mainly attack the cement matrix of the concrete.

Acids dissolve almost every component of the cement matrix (CSH-phases, $Ca(OH)_2$) while forming soluble Ca-, Al- and Fe-salts and silicic acid. The calcium hydroxide ($Ca(OH)_2$) produced to 15-25% mass percentage during the hydration of Portland cement (CEM I) is particularly acid-soluble. During the hydration of cement, calcium hydroxide crystallises primarily in those areas that were previously taken up by the mixing water and on the surface area of the aggregates. This results in the formation of a three-dimensionally linked $Ca(OH)_2$-structure through the whole of the concrete.

Figure 4 shows the polarisation microscopic image of a cement matrix. The CSH-phases and cement clinker are black, the $Ca(OH)_2$ is light-coloured (yellow).

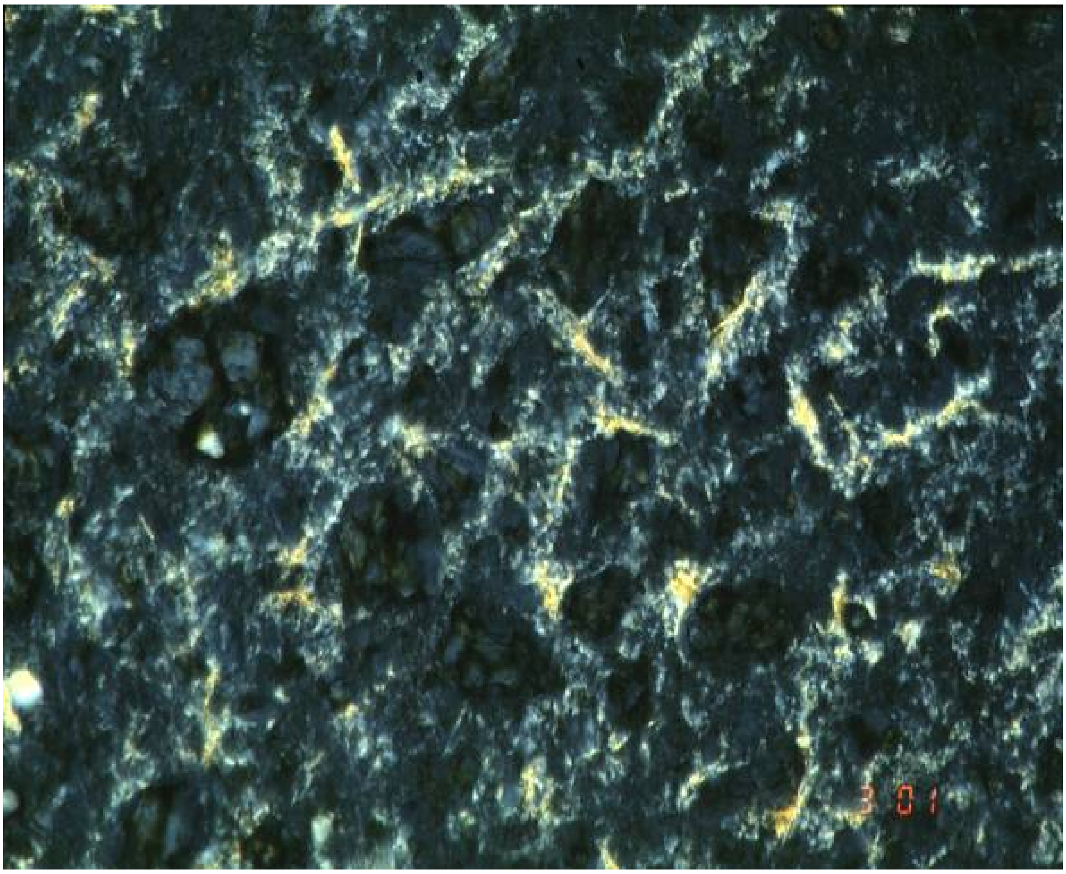


Figure 4: PolMi-image of the three-dimensionally linked calcium hydroxide structure. CSH phases, cement clinker: black; calcium hydroxide: light-coloured

If the calcium hydroxide is solved by an acid, the dissolution quickly proceeds along these paths into the centre of the binder matrix. Initially, the resulting damage to the concrete is not visible.

A further reason why concrete is affected so rapidly by an acid is the Grotthuss transport mechanism for H^+ ions (acid ions). Conventional ions, such as sulphate ions, diffuse through a solution along the concentration gradient. Thus, the ions have to move from the point of origin to the surface of the substrate during the diffusion process. In contrast,

H^+ ions “attach“ themselves to existing water molecules and form H_3O^+- ions. The H_3O^+ ions themselves do not diffuse along the concentration gradient, but give off their “surplus“ H^+ ion to an adjacent water molecule. The result is a transport of H^+ ions, during which the H^+ ions “jump“ from one water molecule to the next along the concentration gradient (bucket chain principle). The Grotthuss transport mechanism is virtually independent of the counter diffusion of solved parts of the matrix and up to 5 times faster than the conventional diffusion of ions.

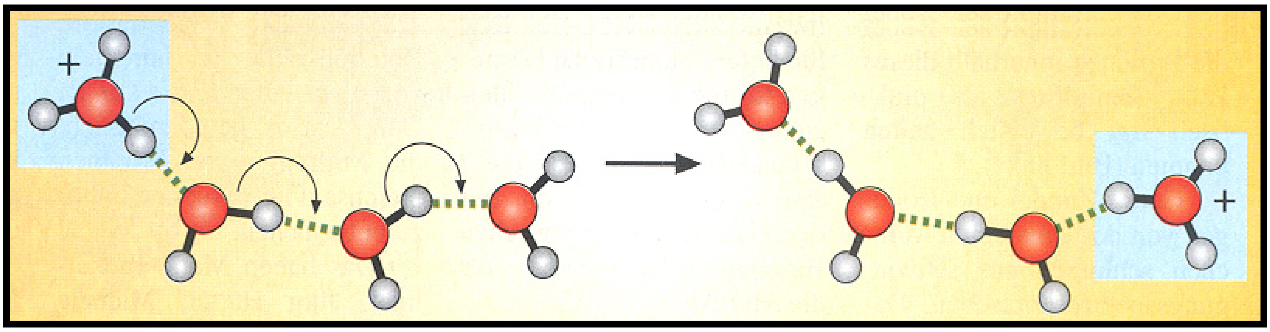


Figure 5: **Grotthuss transport mechanism for H+ ions (acid ions).**

During biogenic corrosion by sulphuric acid, the second step is the diffusion of the sulphuric acid’s sulphate ions into the concrete along the solved $Ca(OH)_2$ paths, where they further destroy the concrete in an expanding attack.

The concrete matrix, which is damaged by (biogenic) sulphuric acid (H_2SO_4), therefore has two damage fronts. Within the first damage front, seen from the damaged surface, the concrete matrix is completely destroyed by solving (H^+) and expanding (SO_4^{2-}) attack. This completely destroyed layer can be removed fairly easily by mechanical means, if it doesn’t fall off of its own accord.

A second damage front, which runs deeper, is invisible to the human eye and can only be detected microscopically. Within this second layer the acid has damaged the concrete matrix merely by solving attack. The mechanical durability of this layer has largely been preserved, as there has been no (or hardly any) expanding attack yet. As the acid hits unhydrated cement clinker, this begins to hydrate, too. This process leads to a change in volume which results in the formation of microcracks. Furthermore, the hydration releases alkalines which counteract the lowering of the pH-value by the acid. Thus, this damage front can neither be detected by a sulphate analysis of drilling powder nor through the use of phenolphthalein.

Figure 6 shows mortar damaged by sulphuric acid viewed under a scanning electron microscope (backscattered electron image). The two damage fronts are visible.

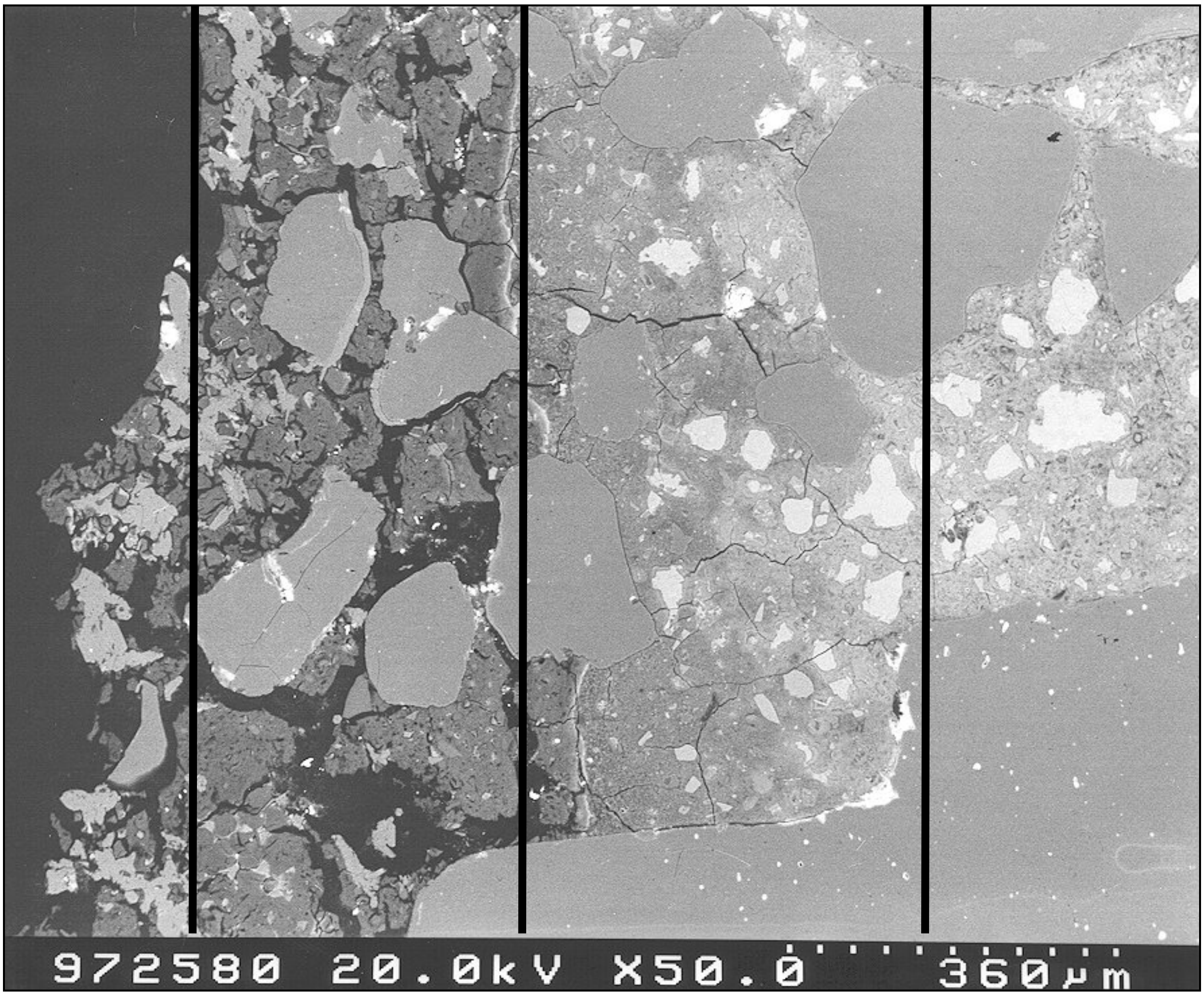


Figure 6: Scanning electron microscopic image of mortar damaged by sulphuric acid (backscattered electron image) with both damage fronts visible. Aggregates (dark grey). White: Unhydrated cement clinker.

If the concrete is not removed to a sufficient depth in the course of reconstruction measures and if the attack by the acid deep within the concrete is not removed completely, the corrosion protection system applied to the concrete or the re-profiling will possibly fall off after a couple of months. The reason for this is that the high pressure water jet, which is usually used to remove damaged areas of concrete, releases the sulphate from the plaster within the first, completely destroyed damage front, which then reaches the deeper, damaged areas of the concrete full of cracks. After the re-profiling or the corrosion protection coating is applied, additional plaster is formed, which can push away the re-profiling or the corrosion protection coating in an expanding attack.

Furthermore, the attack deep within the concrete remains invisible for a long time, because the layer of plaster which is formed makes the concrete appear undamaged. Only after approx. 2 to 4 years of continuous damage will the completely destroyed outer layer fall off, and the first damages become visible. The process begins anew, so that the further progression of corrosion again does not become visible until 2 to 4 years later. During the respective intermediate phases no progression of corrosion is visible.

At the MPA BB a testing method has been developed with which the durability of concrete, or rather the depth of the damage, can be determined exactly.

To assess the durability of concrete comparatively for the development of new sewage systems, test objects are exposed to sulphuric acid with simultaneous simulation of an abrasive attack in a custom-built system over the course of 3 months. Durability is analysed via the microscopic measurement of the attack depths and the further attack by acid deep within the concrete.

The damage of concrete in existing sewage systems is likewise assessed via the microscopic measurement of the attack depths and the further attack by acid on drilling cores.

In both cases the attack depths are determined on microsections using a stereomicroscope. The attack by acid deep within the concrete is determined using a polarisation microscope or scanning electron microscope (backscattered electron image) on thin sections.

Limiting values of acid and sulphate exposure for concrete

DIN EN 206-1, table 2 states, among other things, the limiting values for SO_4^{2-} concentration and the pH-value for an external groundwater attack on concrete (see Table 3). These limiting values apply in case the attacking medium is supplied continuously by the groundwater. According to DIN EN 206-1, Table 3, much higher limiting values apply for affected soil, as the attacking medium is not supplied continuously and for the most part is used up quickly through being bound (sulphate) or buffered by the concrete (sulphate).

Table 3: External corrosion by groundwater according to DIN EN 206-1 (extract from table 2)

Corrosion by groundwater	**Exposition classes for chemical attacks**		
Chemical property	XA1	XA2	XA3
SO_4^{2-} in mg/l	200 to 600	> 600 to 3000	> 3000 to 6000
pH-value	6,5 to 5,5	< 5,5 to 4,5	< 4,5 to 4,0

The most restrictive value for each chemical property determines the exposition class.

In exposition class XA3 (sulphate concentration > 3000 mg/l or pH-value < 4,5) or above concrete must be protected by anti-corrosion systems.

According to the ATV-M 168 guideline, which is in effect only in Germany, the limiting values and requirements for concrete shown in Figure 4 apply to internal corrosion by communal wastewater.

Table 4: Internal corrosion by communal wastewater according to ATV-M 168

Internal corrosion	**Limiting values for…**			
Chemical property	continuous exposure	temporary exposure	short-term exposure	if the following requirements for concrete are met
SO_4^{2-} in mg/l	≤ 600	≤ 1000	no limitation	as below without HS cement
	< 3000	≤ 5000		as below with HS cement
pH-value	≥ 6,5	≥ 5,5 for inorganic acid ≥ 6 for organic acid	≥ 4	w/z ≤ 0,50 and depth of water penetration (DIN 1048) ≤ 3 cm

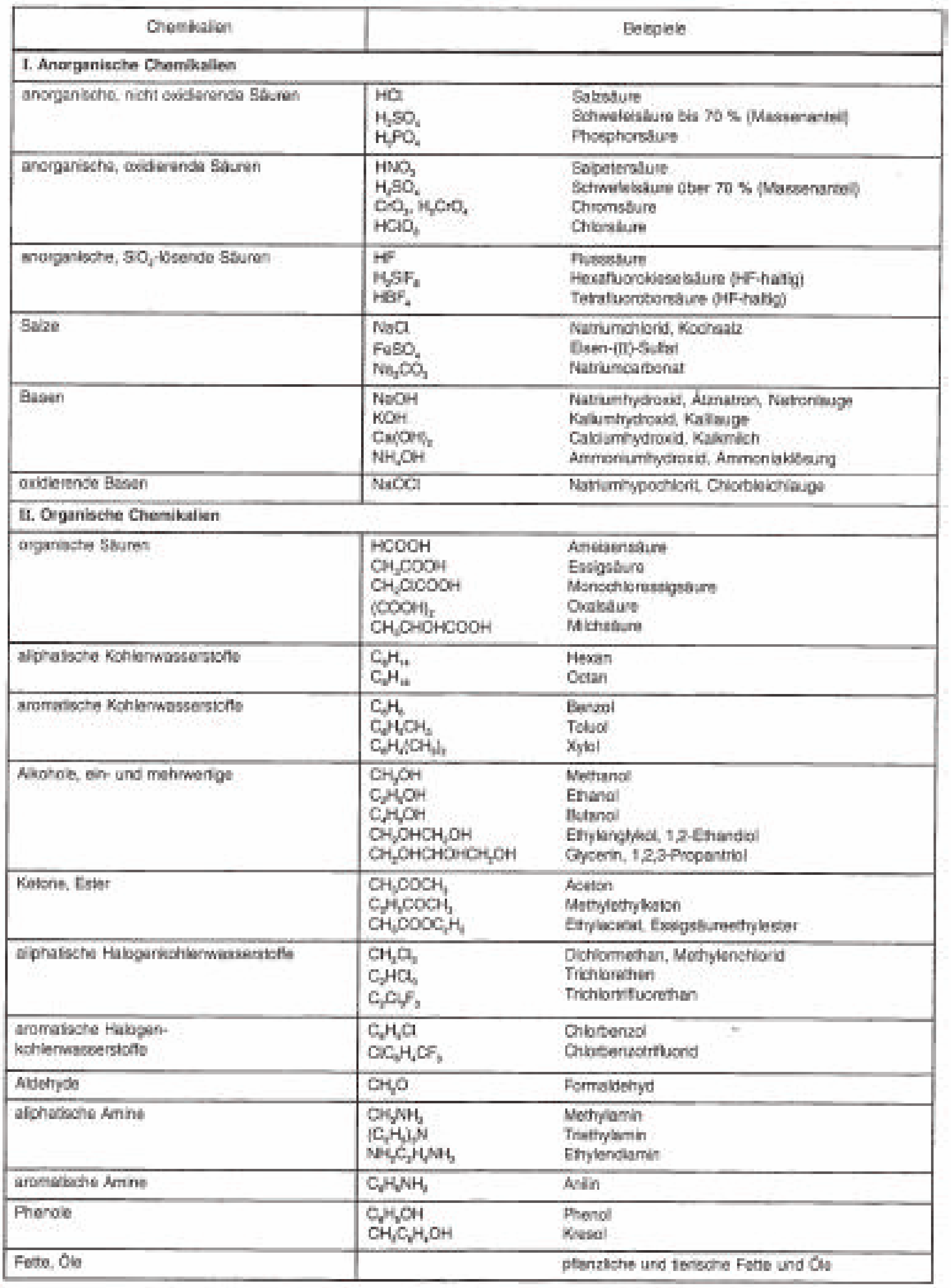
The most restrictive value for each chemical property determines the requirements.

According to ATV-M 168, concrete (with HS cement) needs additional protection by corrosion protection systems if the sulphate concentration is > 5000 mg/l or the pH-value is < 5,5 (long-term exposure).

2.4 Plastic corrosion

A chemically corrosive attack on plastics is caused primarily by organic substances; in principle, oxidizing, strong acids can have corrosive effects as well. The following Table 5 lists chemicals frequently used in industry and trade.

Table 5: Chemicals frequently used in industry and trade according to DIN 28052-1



Chemikalien	Beispiele	
I. Anorganische Chemikalien		
anorganische, nicht oxidierende Säuren	HCl	Salzsäure
	H_2SO_4	Schwefelsäure bis 70 % (Massenanteil)
	H_3PO_4	Phosphorsäure
anorganische, oxidierende Säuren	HNO_3	Salpetersäure
	H_2SO_4	Schwefelsäure über 70 % (Massenanteil)
	CrO_3, H_2CrO_4	Chromsäure
	$HClO_3$	Chlorsäure
anorganische, SiO_2-lösende Säuren	HF	Flusssäure
	H_2SiF_6	Hexafluorokieselsäure (HF-haltig)
	HBF_4	Tetrafluoroborsäure (HF-haltig)
Salze	$NaCl$	Natriumchlorid, Kochsalz
	$FeSO_4$	Eisen-(II)-Sulfat
	Na_2CO_3	Natriumcarbonat
Basen	$NaOH$	Natriumhydroxid, Ätznatron, Natronlauge
	KOH	Kaliumhydroxid, Kalilauge
	$Ca(OH)_2$	Calciumhydroxid, Kalkmilch
	NH_4OH	Ammoniumhydroxid, Ammoniaklösung
oxidierende Basen	$NaOCl$	Natriumhypochlorit, Chlorbleichlauge
II. Organische Chemikalien		
organische Säuren	$HCOOH$	Ameisensäure
	CH_3COOH	Essigsäure
	$CH_2ClCOOH$	Monochloressigsäure
	$(COOH)_2$	Oxalsäure
	$CH_3CHOHCOOH$	Milchsäure
aliphatische Kohlenwasserstoffe	C_6H_{14}	Hexan
	C_8H_{18}	Octan
aromatische Kohlenwasserstoffe	C_6H_6	Benzol
	$C_6H_5CH_3$	Toluol
	$C_6H_4(CH_3)_2$	Xylol
Alkohole, ein- und mehrwertige	CH_3OH	Methanol
	C_2H_5OH	Ethanol
	C_4H_9OH	Butanol
	CH_2OHCH_2OH	Ethylenglykol, 1,2-Ethandiol
	$CH_2OHCHOHCH_2OH$	Glycerin, 1,2,3-Propantriol
Ketone, Ester	CH_3COCH_3	Aceton
	$C_2H_5COCH_3$	Methylethylketon
	$CH_3COOC_2H_5$	Ethylacetat, Essigsäureethylester
aliphatische Halogenkohlenwasserstoffe	CH_2Cl_2	Dichlormethan, Methylenchlorid
	C_2HCl_3	Trichlorethen
	$C_2Cl_3F_3$	Trichlortrifluorethan
aromatische Halogenkohlenwasserstoffe	C_6H_5Cl	Chlorbenzol
	$ClC_6H_4CF_3$	Chlorbenzotrifluorid
Aldehyde	CH_2O	Formaldehyd
aliphatische Amine	CH_3NH_2	Methylamin
	$(C_2H_5)_3N$	Triethylamin
	$NH_2C_2H_4NH_2$	Ethylendiamin
aromatische Amine	$C_6H_5NH_2$	Anilin
Phenole	C_6H_5OH	Phenol
	$CH_3C_6H_4OH$	Kresol
Fette, Öle		pflanzliche und tierische Fette und Öle

Organic solvents are typical organic compounds with a wide range of uses. These substances are employed in technical products or processes, but can also be found in many ordinary household products.

Small amounts of organic solvents reach the sewage systems as part of industrial or private wastewater. Large amounts of solvents in sewage systems can be caused by accidents or deliberate illegal disposal.

Depending on the location and the history of the soil, these substances can also affect the construction material of sewage systems externally. In possibly polluted areas (i. e. on former sites of the metal-working or chemical industry, or of petrol stations) heavy pollution with the compounds mentioned above, especially aromatic or chlorinated hydrocarbons, can occur. As these are practically water-insoluble, even large amounts of hydrocarbon will lead to only small amounts in the water phase, while the remainder forms a fluid plume which remains above or below the groundwater, depending on its density. Within these plumes of harmful substances, the hydrophobic hydrocarbons are thus virtually undiluted. Therefore, the effect of organic solvents on the construction material of sewage systems has to be examined both from the inside of the pipe as well as from the outside.

Whereas the attack on the outside of the pipe can be expected primarily from the liquid phase, an attack from the gas phase must be considered inside the pipe, because all substances in this group are more or less volatile.

Among the compounds with especially high relevance with regard to the amount of the substance or the corrosive effect on plastics are most notably:

- halogenated hydrocarbons
- aromatic hydrocarbons

The MPA Berlin-Brandenburg is involved in the planning work for the materials to be used in the Emscher canal in North Rhine-Westphalia, which is presently the largest wastewater construction project in Europe, with a total investment volume of 4,5 Billion Euros. In the course of the evaluation phase, various studies were conducted to assess the risk of corrosion in sewage systems.

Wastewater and groundwater analyses indicate that the corrosion of plastics (pipes and seals, for example) by aromatic and halogenated hydrocarbons must be taken into account in sewage systems located in industrial and densely populated areas.

During the loading of aromatic or halogenated hydrocarbons to plastics or plastic systems it could be observed that many of the standard plastics for sewage systems showed considerable corrosion to the point of complete disintegration after only a few hours. An example is shown in the following image.

Figure 7: Front: GFK-specimen stored in halogenated hydrocarbons for 14 days. The plastic has dissolved, merely the glass fibres remain.
Back: Specimen without loading for comparison

An unexpected result was that the rapid disintegration after several hours or days of storage in aromatic or halogenated hydrocarbons occurred not only in the liquid phase, but also in the gas phase. Several plastic systems also showed signs of corrosion after storage in sulphuric acid. These facts indicate that plastic corrosion is possibly relevant to the durability of sewage systems.

Figure 8: Various polymer concretes after 20 hours in the gas phase of halogenated hydrocarbons

Based on present experience, an online monitoring system should primarily determine aromatic and chlorinated hydrocarbons.

In the context of a research project of the Emschergenossenschaft-Lippeverband, which was conducted by the Gesellschaft für Materialprüfung und Baustofforschung (MBF) as parent company of the MPA BB in cooperation with the engineering firm Zerna Ingenieure from 2004 to 2006, a test procedure was developed at the MPA Berlin Brandenburg with which the corrosion of plastic corrosion protection systems by hydrocarbons or sulphuric acid (as well as all other relevant corrosive substances) can be determined.

Chapter 3

Measurement

3.1 Introduction

Online monitoring, within the scope of a pilot plant, should allow for a most comprehensive acquisition of relevant test measurement parameters, associated with formation and occurrence of the activity of odour and/or of corrosion substances or groups of correlated substances.

As discussed in sec. 2, depending on the material of technical wastewater facilities, mainly following substances or groups of substances are active corrosives:

- Plastic material ↔ primarily damaging: halogenated hydrocarbons, aromatic hydrocarbons
- Concrete material / reinforced concrete ↔ primarily damaging: sulphuric acid, (nitric acid)
- The main parameter for odour in wastewater facilities is H_2S.

The following Table 6 presents the odour-active and corrosion-active substances for plastics and concrete as well as the essential ones participating on their formation and shows where they appear (wastewater, gas, biofilm, pipe material).

In an additional row (desirable to measure) an estimation is made where (wastewater, gas, biofilm, pipe material) it is meaningful to carry out detection tests for odour- and corrosion-active substances or participating substances in their formation, by sensors (for modelling).

Table 6: Corrosive compounds, their causing parameters, precursors and reaction product and importance to measure

Corrosive Compound	Sewage	Gas	Biofilm	Material
Plastics				
Organic solvents	+	++	0	
Desirable to measure	+	++	-	
Concrete				
Sulphuric acid: (H_2SO_4)	$O_{2,}$ org. sulphuric compounds, SO_4^{2-}, HS^-, S^{2-}	H_2S (odour)	acid (H_3O^+), sulphate (SO_4^{2-}), bioactivity	gypsum, pH-value
Desirable to measure	+ (O_2, $SO_4^{2-}S^{2-}$)	++	++ (acid) + (sulphate)	+ (pH-value)

Parameters for Corrosion of Plastic

Primarily, organic compounds have damaging effects, especially chlorinated hydrocarbons and aromatic carbons, which in turn are used as common solvents. Because the last mentioned compounds largely show low solubility in water, it can always be assumed, when they are present that they are inhomogeneously distributed in wastewater (phase separation).

A representative, continuous detection in wastewater would therefore always make a preceding homogenization necessary, which would always mean a massive intervention in the equilibrium between the liquid and gas phase (e.g. for $HS^-/S^{2-}_{liquid} \leftrightarrow H_2S_{gas}$).

In addition, after homogenization, organic compounds must be separated from the water again, as most detection methods for organic compounds react sensitively to water or are even damaged by it. Due to this fact and the volatility of most of the organic compounds, detection in the headspace of the technical wastewater plant appears to make most sense.

A sensory compilation, taken directly on the ground of technical wastewater plants (below the sewage line), only makes sense for halogenated hydrocarbons with a higher density than water.

Parameters for Corrosion of Concrete

Material damages to the concrete are caused mainly by sulphuric acid that is formed in the biofilm around the headspace of wastewater systems. Primarily the acid (protons) damage the concrete by a dissolving attack, secondary damage is done by sulphate ions through an impellent attack.

For the investigation of potential danger of concrete corrosion, the measurement of the pH-value directly on the concrete surface in the biofilm is essential, subordinated is the detection of sulphate ion concentration in the biofilm. For the investigation of an ongoing concrete corrosion, knowledge of the decrease of pH-value in concrete would be important.

Parameters for Odour

A practice-designed online monitoring system must – additionally to the methods described before - at least measure the gas H_2S which is mainly responsible for the unpleasant odours. As well as the acid concentration in the biofilm and the concentration of halogenated and aromatic hydrocarbons in the head space, the concentration of H_2S has to be captured in order to ascertain the current condition of the wastewater systems regarding corrosion and odour.

Parameters for Modelling

For understanding of occuring processes and modelling, in addition to the “primary” substances that are responsible for odours and corrosion, there are more parameters to be captured in order to determine the relationship to chemical and biological processes in practice or in a simulation system under various conditions.

According to chemical and biological processes, that lead to the development of sulphuric acid in the biofilm of the gaseous phase, by using the key precursor H_2S provided by sulphur and sulphate compounds in the wastewater under anaerobic conditions, it would make sense, to determine the precursor and intermediate products online: concentration of sulphurous organic compounds, sulphates and sulphides in wastewater and H_2S in the headspace.

Since redox processes play the essential role for metabolization of sulphur compounds, the redox potential of the wastewater and biofilms and the oxygen concentration in the system are also to be determined. In particular, the oxygen content in the effluent is a key indicator.

Naturally, the organic load of wastewater has the main influence on biological activity in wastewater and indirectly on the biofilm. The main parameters for identification of organic load are BOD and COD. These parameters should be regularly surveyed in sewage. Since the metabolic activity of biofilms is responsible for the formation of active corrosive sulphuric acid, determination of biological activity of biofilms is important.

The chemical and biological processes also depend heavily on the physical boundary conditions such as temperature, air pressure, flow velocity, or mass flow. That is why the most comprehensive measurement of these parameters for modelling is important.

The same considerations as in the case of sulphuric acid can be made for the formation of nitric acid from nitrogen precursors. Due to the lower relevance of the biogenesis of nitric acid and thus substantially limited relevance both in the case of odour and corrosion, the screening of the nitrogen compounds are of less importance. Their relevance rises, if dosage of nitrate is applied as countermeasure.

Table 7 shows the parameters, which have to be measured to determine the relationship of chemical and biological processes in the practice, or in a simulation system under various conditions.

Table 7: Necessary parameters for determination of relationships of chemical and biological processes in wastewater systems

Parameter/ Medium	Sewage	Air	Biofilm	Pipematerial
pH	x	x	x	x
Temperature	x	x		x
Redox potential, O_2-conc.	x		x	
organic load: BOD and COD	x			
S-species: sulphate			x	
organic bound sulphur	x			
hydrogen sulphide	x	x		
N-species: HNO_3		x	x	x
nitrate, nitrite	x			
organic solvents		x		
concentration of applied chemicals	x	x		
biological activity			x	
velocity, flow	x	x		
moisture		x	x	

3.2 Existing Sensor Technology

In the following a summary of sensors is given that are currently available for the described parameters. If available continuously measuring systems are described as well. The systems are classified by the medium in which the measurement can be carried out (sewage – headspace – biofilm – material). The same characteristics are selected for the description of practicability with all measurement principles. If for one of the characteristics no indication is given, there is no information available.

3.2.1 Measurement in Sewage

3.2.1.1 pH-value

ISFET pH-meter

Functionality

ISFET stands for ion sensitive field-effect transistor. Analogue to the general field-effect transistor (FET) the measurement principle is based on the change of the field effect (training of a space-charge zone) between SOURCE and DRAIN. The function mode of FET is not described in the following. It is expected to be familiar. In place of the electrical contact at the GATE a pH-sensitive layer with the ISFET (ex. Ta_2O_5) applied, which is brought directly in contact with the measured liquid. Over a bias voltage, which is applied over a reference electrode, which likewise is in the solution, the operating point of the ISFET can be specified analogue to the establishment of the operating point of a FET. Dependent on the concentration of the ions in the solution which can be examined, an additional surface barrier at the contact between liquid and ion sensitive layer (Nernst equation) is formed. This potential adds itself on the constantly applied bias voltage and affects thus the space charge zone between SOURCE and DRAIN. This leads to a change of the SOURCE drain stream, which can be measured. The changes are directly proportional therefore to the change of the analyte concentration. Over a calibration, can be reckoned back, with help of the measured river on the analyte concentration. The ISFET is electrically regarded thereby as a trans-impedance transducer. An electrical potential is measured potentiometrically, without considerable current, and it is converted into a measurable SOURCE-DRAIN-current. This is in first approximation independent of following circuits and thus as high impedance „power source “ [GRÜNDLER, 2003].

Practicability

There are sensors available on the market for measurements in the wastewater system which are compiled in the following table:

	Emmerson Process Management TFS396	**Knick, pH-Sensor SE 545**
Measurement range	2-12 pH	0-12 pH
Accuracy	±0,05 pH	
Speed of response	99% within 30 sec. after pH-change	
Materials process tangent	stainless steel 1.4401, Polypropylene, EPDM, Ryton, Silicone	PEEK, Elastomeric EPDM
Allowed process temperature	0 to 100 °C @ 3,45 bar	0 to 80°C @ 6 bar
Allowed process force	-0,65 to 6,9 bar @ 50 °C	0 to 6 bar @ 80°C
Minimal allowed process conductibility	75 µS/cm nominal 100 µS/cm	

Specific literature:

Emerson Process Management / Rosemount Analytical: PDS49-TFS396 Rev. C http://euedocs.emersonprocess.co.uk/groups/public/documents/markcom/pds_ph_tfs396_rev_c.pdf

Knick, Produktkatalog 2007, http://www.knick.de/

Galvanometric pH-meter

The pH meter is a standard device for measuring pH-values of samples. It is mainly used in laboratories for discrete measurements. There are pH-meters that can be applied continually.

Functionality

A glass diaphragm ball filled with a potassium chloride solution is immersed into the liquid that is measured. By the inclination of the hydrogen ions to deposit itself in thin layer at the glass surface a galvanic voltage develops itself inside the ball. A galvanic cell is developed, whose electric motor force is relative to a reference electrode independent of the hydrogen ions one measures [SCHWABE, 1976; BATES, 1954; HÖLL, 2002; DEV, 2003].

Practicability

For continuous application, special electrodes are available, which are characterised by increased robustness. The following table arranges the characteristic values of a selection of such sensors:

	Driesen&Kern, pH-Log530	**Hach Lange, pH-/Redox-Kombi-Elektrode 8350**	**Bürkert, pH-Sensor 8201**	**WTW, ph-Einstabmesskette Sensolyt SEA**
Measurement range	1...14 pH	0…14 pH	0…10 pH	2…12 pH
Accuracy	0,02 pH	0,05 pH	0.1 pH	
Speed of response				
Material tangent	Casing V4A	PTFE-compound, safety glas, PPS case	Enamelled steel pipe, Ground diaphragm ceramic enamelled, Process connection 1.4404, Electrode head PVDF, Seal EPDM	
Allowed process temperature	0,2°C...+80°C	max 110°C	0 to +140°C	
Allowed process force		10 bar @ 80°C	-1…6 bar rel.	< 10 bar @ 20°C, < 1bar @ 60°C
Comments	Data logger with integrated power source designed for field use in river monitoring Pt-temperature measurement with automatic compensation	Temperature compensation		Mounting in special Sensolyt-mounting

Specific literature:

{ Driesen & Kern, pH-Log530, http://www.driesen-kern.de/downloads/phlog530.pdf }

{ Hach Lange, ph-8350, Angebotskatalog 2007, Angebot 194460, S. 53-56 }

{ Bürkert, pH-Sensor 8201, http://www.buerkert.com/products_data/datasheets/DS8201-standard-EU-EN.pdf [2007-09-07] }

{ WTW, pH SEA, Katalolg Online Messtechnik 2006, S.18}

Thick Film pH Sensor

The thick film pH sensor was developed by the Fraunhofer Institute of Ceramic Technologies and Systems in Dresden. Even after demand there was hardly any further disclosures of information to the sensor made available.

Functionality

The thick film pH sensor consists of a sturdy mother board of steel which is isolated. On the isolation layer in the thick-film procedure on one side the test electrode, on the other side the reference electrode is attached. The sensor works like a pH meter, gets along however without liquid system components. It is pressure insensitive and compatible to commercial pH measuring instruments.

Practicability

The ranges of application which are named for the sensor are the chemical industry, food technology and medical technology. Its potential strength is shown in the economical fabrication as well as in its break resistance and the adaption possibility of the sensor layout because of the requirements of application. An application in wastewater is not described and must be exactly examined. A commercial manufacturer is not known.

	Thick Film pH Sensor
Measurement range	1…9 pH
Accuracy	0,3 pH
speed of response	< 1s
Allowed process temperature	25 – 55 °C
Comments	drift < 2mV/d (<0,04 pH/d), drift reference electrode < 1mV/d

Specific literature:

{Fraunhofer-Institut für Keramische Technologien und Systeme, Informationsblatt Thick Film pH-Sensor, Messestand Sensor+Test, Nürnberg 2007}

3.2.1.2 O_2-Concentration

Oxygen is present both in the gaseous phase in gas form and in the wastewater in dissolved form. The respective concentrations are determined by sensory measurement. Measurement principles are described below. For the description of the practicability with all presented measurement principles the same characteristics were selected. If to one of the characteristics no indication is given, no information is present for this.

Clark-Oxygen Electrode

The main application range of Clark oxygen electrodes lies in the regulation of oxygen concentration in liquids. Lesser represented, although also feasible, is the measurement if oxygen concentration is in gas mixtures.

Functionality

The Clark-electrode consists usually of a platinum cathode and a silver anode as reference electrode, which stands over an electrolytic solution connection. They are separated by an oxygen-permeable diaphragm from the sample. On the platinum cathode a bias of -0,8 V rests against the silver anode.

If one brings the solution which can be examined to the measuring chamber now to the diaphragm, then the CO_2 partial pressure difference between diaphragm outside and inside to a CO_2 diffusion leads by the diaphragm foil into the measuring chamber. The oxygen is reduced at the cathode, takes up thus electrons of the cathode, whereby hydroxyl ions (OH^-) are developed. At the anode to Silver chloride one oxidizes to silver, therefore an Ag/AgCl electrode is also usually used.

Cathode: $O_2 + 2\ e^- + 2\ H_2O \rightarrow H_2O_2 + 2\ OH^-$ und $H_2O_2 + 2\ e^- \rightarrow 2\ OH^-$

Anode: $4\ Ag \rightarrow 4\ Ag^+ + 4e^-$ und $4\ Ag^+ + 4Cl^- \rightarrow 4\ AgCl$

The result is thus a current, which is directly proportional to the partial pressure p of the oxygen CO_2. This current is measured and becomes back-closed on the concentration of the oxygen.

Since the oxygen solubility and the permeability of the diaphragm are temperature-dependent, compensation is necessary [HAMANN & VIELSTICH, 1985; GRÜNDLER, 2003; RUMP, 2003; HÖLL, 2002; DEV, 2003].

Practicability

The application in wastewater, sensors were developed which are especially protected against contamination. The following table arranges some sensors. No data mean that no information is present.

	Knick, Sauerstoff-Sensor SE 703	**WTW, TriOxmatic 700**	**Hamilton, Oxysenes**	**Ahlborn, FYA640O2**
Measurement range	pO2 < 1200 mbar	0…60 mg/l	40ppb … saturation	0,0…40mg/l
Accuracy	1 % + 30 ppb	0,1 mg/l		< 1%
Detection limit	30 ppb			
Response time at 25 °C (Air –> N2)	98 % of final value < 90 s	t90 < 180 s	t98 < 60 s	t90 < 15s
Signal in Air	40 … 110 nA			
Residual signal in O2-free medium	≤ 0,3 % of signal in air			
Flow dependency	≤ 5 %		≤ 5 %	
Pressure range	0,5 … 2 bar absolute	< 10 bar	0…4 bar	
Temperature range	0 … 60 °C	0...50°C	0…60°C	-5..50°C
Material process tangent	Silicone and FKM (Viton), Membrane: PTFE/Silicone/ PTFE (Steel-net reinforced), PPS			
Frequency of necessary re-calibration			Sensitivity shift < 10% every 2 months with 25°C water and stable conditions	
Durability				Operating time with single Electrolyte filling: several months, Total: several years
Comments		Reference-Electrode increasing signal stability and self-monitoring of electrolyte replacement		

Specific literature:

{Co Knick Berlin, Sauerstoff-Sensor SE 703, http://www.knick.de/hps/ client/knick/public/ index.hbs }

{Co WTW, WTW – Welt der online Messtechnik, http://www.wtw.com}

{Co Hamilton, http://www.hamiltoncompany.com/eu-sensors/oxysens.asp}

{Co Ahlborn, Gesamtkatalog Ausgabe 2007/2008, S. 15.08}

Fibre-optic Sensor

In the last decade a large number of measuring procedures have emerged from the range of fibre optics. Thereby, the absorption and fluorescence characteristics of materials are used in dependence of the light wave length as well as the change of refraction characteristics of the light conductor with accumulation of certain materials within ranges of the conductor.

For the measurement of oxygen, this principle of measurement can be applied both in the gas phase and for the measurement of liquids.

Functionality

The fibre-optic oxygen sensors are coated probes that use fluorescence quenching to measure the partial pressure of dissolved or gaseous oxygen. Different sensing formulas are available (ruthenium or Pt-porphyrin formulation). The system works like this:

An LED sends excitation light to one leg of a bifurcated optical fibre assembly. The fibre carries the light to the oxygen probe, which is polished to a 45° angle. The distal end of the probe tip consists of sensor formulation trapped in a sol-gel matrix, immobilized and protected from the sample. The light from the LED excites the ruthenium or pophyrin sensor formulation at the probe tip. The excited complexes fluoresce, emitting energy at ~600 nm and 650nm, respectively.

If the excited complex at the probe tip encounters an oxygen molecule, the excess energy is transferred to the oxygen molecule in a non-radiative transfer, decreasing or quenching the fluorescence signal. The degree of quenching correlates toe the partial pressure of oxygen in the sol-gel, which is in dynamic equilibrium with oxygen in the sample.

The fluorescence is collected by the probe and carried to the Spectrometer/MFP Fluorometer via the second leg of the bifurcated optical fibre assembly.

The following assemblies are available:

Oxygen sensor with spectrofluorometer:

Oxygen is sensed by measuring the decrease in fluorescence intensity of a fluorophore bound to the tip of an optical fibre. The sensor responds to the partial pressure of oxygen.

Oxygen Sensor with multi-frequency Phase Fluorometer(MFPF):

Oxygen is sensed by measuring the phase shift of fluorescence of a fluorophore bound to the tip of an optical fibre. The sensor responds to the partial pressure of oxygen.

{cp http://oceanoptics.com/Products/catalogsensors.pdf [2007-09-07]}

Practicability

In the following table characteristic values are arranged for a fibre-optic measuring system. The characteristic values refer to the assigned indicator matrix. The advantages of the procedure are independent from changes in the pH-value, amount of salt and ionic strength. There is no influence by humidity, CO_2 or methane.

	Ocean Optics, FOXY Sensor Formulation	**Ocean Optics, HIOXY Sensor Formulation**	**Hach-Lange, Lange LDO- Sensor LXV416.00.00001**
Measurement range	0-40 ppm (dissolved), 0-100% (mole percent)	0-40 ppm (dissolved), 0-100% (mole percent)	0.05 to 20 mg/l 0.05 to 20 ppm
Accuracy	0.02 ppm, 0.05%	0.02 ppm, 0.05%	0.01 mg/l, 0.01 ppm, 0.01 % saturation 0.1 °C
Detection limit	0.02 ppm (dissolved), 0.05 %	0.02 ppm (dissolved), 0.05 %	
Response time at 25 °C (Air –> N2)	< 45 s	< 1 s	T 90% < 30 s, programmable
Allowed process temperature	-50…80 °C	-50…80 °C	0 to 50 °C
Frequency of necessary recalibration			Not necessary Air or inline calibration possible
Durability	Probe: Recondition once per year	Probe: Recondition once per year	One year warranty
Comments	Benign environment, aqueous liquids and vapours	designed for monitoring in non-aqueous fluids: Hydrocarbon-based liquids and vapours, fuels	No interference from the following: H_2S, pH, K^+, Na^+, Mg^{2+}, Ca^{2+}, NH_4^+, Al^{3+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, $Cr^{ges.}$, Fe^{2+},Fe^{3+}, Mn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, CN^-, NO^-, SO_4^{2-}, S^{2-}, PO_4^{3-}, Cl^-, Cl_2, anion active tensides, cruide oils

Specific literature:
{Co http://www.hach-lange.de :: DOC053.52.03203.Apr03}
{Ocean Optics Ltd., http://oceanoptics.com/Products/catalogsensors.pdf [2007-09-07]}

3.2.1.3 Redox Potential

Redox Measuring Chain

The measurement of the redox current takes place with a redox measuring chain. Its structure is similar to the pH meter.

Functionality

Like the pH-measuring chain (pH meter) the redox measuring chain consists of a measuring and a reference electrode. Instead of the glass diaphragm it possesses a metal electrode (usually from a precious metal such as gold, silver or platinum), which take over the measuring function. The inclination of the solved ions to take up or deliver electrons, determines the potential of the test electrode and thus the electrical voltage of the measuring chain. Commercial redox electrodes contain a silver/ silver chloride element as reference electrode. All measured voltage refers to its potential. A conversion on the system of the normal hydrogen electrode (UH) is easily possible:

$U_H = U_{Mess} + U_{Ref}$

Due to the same structure, Redox and pH-measuring chains are often accommodated in the same probe [HAMANN & VIELSTICH, 1981; GRÜNDLER, 2003; RUMP, 2003; HÖLL, 2002; DEV, 2003].

Practicability

Sensors, that are similar to each other, are available from various manufacturers. Two sensors are described exemplary:

	WTW, SensoLyt PtA	**Hach Lange, 1200-S sc Redox**
Electrode type	Gel-Polymer solid electrolyte, double-fold perforated diaphragm	Ag/AgCl Polymer, perforated diaphragm
Measurement range	+/- 2000 mV	+/- 1500 mV
Accuracy		
Response time		t90 < 15s
Material process tangent	Glass membrane, PVC protective shell	Stainless steel, PPS, glass/Platin
Allowed process temperature	0…60°C	-5…60°C
Allowed process pressure	1 bar @ 60°C 10 bar @ 20°C	max 2 bar overpressure

Specific literature:

{ WTW , pH PtA, Katalolg Online Messtechnik 2006, S.18 }

{ Hach Lange, 1200-S sc, Angebots-Katalog, S.46/76 }

{cp http://www.wtw.com/media/LaborundUmweltKatalog2006_I.pdf [2007-09-06] S.22}

3.2.1.4 COD

The sum value of chemical oxygen demand (COD) is a measurement for all in the water existing and under certain conditions oxidizable materials. It indicates the quantity of oxygen (in mg/L) which was needed for its oxidation, if oxygen were the oxidizing agent.

The determination of the COD is usually to be accomplished wet-chemically in the laboratory on the basis of a water test. It is standardized. This process is very complex. For the determination without the complicated chemical process cycle cuvette high-speed tests were developed. These measure the dichromate consumption of the sample of water in the test liquid of a prefabricated cuvette according to a photometric principle.

For the quasi-continuous measurement instruments with a sampling mechanism and automatic analysis are available. A continuous detection is reached using spectrometer probes. With this procedure it will furthermore be dealt with [RUMP, 2003; HÖLL, 2002; DEV, 2003].

Spectrometer Probe

A wide-band spectral measurement is made and reckoned back over correlation functions on the COD content.

Functionality

The probes measure the spectrum from ultraviolet to the long-wave visible light. From the high information content the measured values are determined. The foundation is a long term built up database and the whereupon developed algorithms. The wide-band measurement permits the compensation of the disturbing influence of the turbidity.

Practicability

Sensors are used in sewage engineering and are characterised by the following advantages in relation to other procedures:

- direct measurement in the process medium
- on-line-processing
- precise measurement due to the spectral analysis of the scanned UV/VIS range in place of a punctual measurement
- high durability by automatic compressed air cleaning before each measurement

One disadvantage of the procedure is the indirect measurement and the necessity to fall back to an existing database and algorithms. The selection of used data and methods for correlation has substantial influence on the result and can, with strongly varying wastewater compositions, lead to bad results. Likewise unfavourable is the necessary compressed air connection (3-7 bar) which effects the installation. Such a sensor is offered to

WTW under the designation CarboVis, the most important characteristics are arranged in the following table. A study about process stability for the application of UV-VIS-Systems for sewage and surface water is ongoing at Kompetenzzentrum Wasser Berlin and Institute of Civil Engineering – Department Urban Water Management.

	WTW, CarboVis	**s::can, carbo::lyser™**
Principle of Measurement	Spectral measurement in UV/VIS range: 200 - 750nm	UV-Vis spectrum between 200 and 750 nm.
Measurement range CSB	0.1…800.0 mg/l	5.0...1500 mg/l 5.0
Measurement range TOC	1…500 mg/l	
Accuracy	+/-3 %	+/- 5.0 mg/l
Measurement range solids	0…3000 mg/l (optional)	
Materials	Al Mg Si 1, anodized	stainless steel
Allowed process pressure	<= 1 bar	
Allowed process temperature	0…45°C	0 - 45 °C
Flow velocity	<= 3m/s	
pH-range	4…9 pH	
Salinity of mediums	< 5000 mg/l (Chloride)	

Specific literature:

{WTW, CarboVis, http://www.wtw.com/media/OnlineMessKatalog2006_I.pdf [2007-09-07] S.50ff}

{s::can, Product description http://www.s-can.at/index.php?id=16 }

3.2.1.5 BOD

The laboratory determines the BOD after sampling. There are different methods, which are all based on the biological processes at constant temperature of the sample within the entire time. Subsequently, consummation of oxygen can be calculated in different ways (sometimes collateral). For on-line measurement, these procedures are inadequate, indirect measurements are used [RUMP, 2003; HÖLL, 2002, DEV, 2003].

Spectrometer Probe

A wide-band spectral measurement is made and reckoned back over correlation functions on the BOD value.

Functionality

This is the same principle that also describes the determination of the CSB. The difference in the procedure is only a different underlying data basis and changed correlation methods.

Practicability

The same statements are valid as under sec. 3.2.1.4, since the same sensor for the determination of the BOD_5-value is used. A known sensor is CarboVisTM of WTW.
Specific literature:
{WTW, http://www.wtw.com/media/OnlineMessKatalog2006_I.pdf [2007-09-07] S.50ff}

3.2.1.6 Sulphate

Sulphates are salts or esters of the sulphuric acid. The salts contain as anion the sulphate ion [SO_4^{2-}]. They are chemically proven, by adding hydrochloric acid and barium chloride or barium hydroxide solution. A heavy, soluble precipitation of white barium sulphate is developed [JANDER & BLASIUS, 1980; DEV, 2003; RUMP, 2003].
There is commercial sensor for the detection of sulphates in aqueous solutions available. Research exists, which concentrates on the development of bio sensors. These are, however, still far away from application in the wastewater range. The work is outlined briefly.

„Biosensor using Thiobacillus ferrooxidans“

The research work took place in the late 90's at the University of Tokyo and a sensor was developed with which the sulphate content in rain water can be measured.

Functionality

Thiobacillus ferrooxidans E-15, known to oxidize Fe(II) in the presence of sulphate was immobilized on the surface of an oxygen electrode. The current decrease at the microbial correlates with the sulphate concentration.

Practicability

The response time of the sensor was about 30 min. The strongest response was obtained in an environment of 30°C, the optimal growing temperature of the microbe, and a pH-value of 2.75. The microbe immobilised membrane lost its activity 24h after immobilization. Therefore a renewing of the membrane is necessary each day. The lower limit of detection was 4µM with good measurements in the range of 0-200µM. Nitrate concentration below 200µM and chloride concentration lower than 8.97mM showed no effect on the measurements. The researchers suggested a replacement of the membrane after 15 measurements. They stated the low cost of the microbial membrane. Any further developments are not known.

Specific literature:

{„Sulfate sensor using Thiobacillus ferrooxidans“, Sasaki, Yokoyama, Tamiya, Karube, Karube, Hayashi, Arikawa, Numata , Analytica Chimica Acta 347, pp.275-280, 1997 Elesevier Science B.V.}

3.2.1.7 Sulphide

Sulphides are salts or esters of hydrogen sulphide (H_2S). The sulphide anion (S^{2-}) is shortly named sulphide. The concentration of the anions is to be determined in the aqueous phase.

Ion Selective Measurement

Functionality

The ion-selective measurement is a method relative to the determination of the concentrations of solved ions at small instrument expenditure. Examples of directly in the solutions assignable cations and anions are potassium ions, sodium ions, fluoride or chloride. Indirect procedures like e.g. Titration make the regulation of aluminium ions, nickel ions or sulphate possible. The measurement with ion-selective electrodes is a potentiometric such as the pH-measurement. The following design can be applied:

1. separated ion-selective electrode and reference electrode
2. ion-selective measuring chain with combined inserted reference electrode

Depending upon which ion should be measured, the diaphragm of the measuring chain consists either of a barely soluble salt of this ion (solid electrode) with ion-exchange or ion-carrier modified PVC diaphragm (matrix electrode), glass (glass electrode) or a gas permeable diaphragm (gas sensitive electrode). The activity of the measuring ions determines the voltage of the measuring chain. With rising activity of anions, the tension becomes more negative; with cations more positive. A pH/ion meter computes the concentration value of the solution of the measuring chain signal.

Practicability

There are special sensors for the measurement of sulphide ions in aqueous solutions. The electrodes are offered by different manufacturers. The most important characteristics are the exemplary set up of two exemplary products in the following table. No statements are known about the application in wastewater.

	Radiometer analytical, ISE25S	**WTW, ISE Typ Ag/S 800**
Concentration range (M)	5 x 10-7 – 100	10-7...1 mol/l
Concentration range (ppm)	0.02 – 30000	0,003...32000 mg/l
Temperature range	0 – 60°C	
Diameter	12 mm	
pH range	11 – 14 (direct meas.)	2-12
Sensor type	Solid-state	Solid-state
Interfering ions	Equally sensitive to Ag+, Precipitated cations forming complexes with sulphides	
Recommended reference electrodes		reference electrode incl.

Specific literature:

{Radiometer analytical, ISE25S, “MeterLab Guide to Reliable pH, Ion and Conductivity Measurements (Electrodes) Data Sheet (lit 4416) “, http://www.hach.com/fmmimghach?/CODE%3AL4416_01-0712747%7C1}

{WTW, ISE Ag/S, http://www.wtw.com/media/LaborundUmweltKatalog2006_I.pdf [2007-09-06]}

{http://www.wtw.com/media/LaborundUmweltKatalog2006_I.pdf [2007-09-06]}

3.2.1.8 Organically Bound Sulphur

There is no information about sensors for the determination of organic sulphur in wastewater. The determination can only be carried out in laboratories.

3.2.1.9 Nitrate and Nitrite

Nitrates are the salts and esters of nitric acid (HNO_3). Nitrites are the salts and esters of nitrous acid (HNO_2). NO_2-and NO_3 anions are identified in wastewater.
{cp http://de.wikipedia.org/wiki/Nitrat , Nitrit}

Ion Selective Measurement

With this procedure nitrate concentrations are assignable in wastewater.

Functionality

The principle works potentiometrically with a measuring and a reference electrode. The function mode of the ion-selective measurement is identical to section 7.1 which has been described.

Practicability

Electrodes are available on the market for the measurement of nitrate. The characteristics of some products are summarized in the following table.

Since the ion-selective electrodes are affected by interfering, it makes sense to compensate disturbances. The firm WTW has developed the product "VARiON sensor that the installation of various electrodes and thus allows compensation for the nitrate measurement, the chloride ions. This sensor was constructed especially for measurement in wastewater.

	Radiometer analytical, ISE25NO3	**WTW, VARiON NO3, Kompensiert VARiON Cl**
Concentration range (M)	3 x 10-6 …100	0,5 … 4500 mg/l [Cl-: 1 ...1000 mg/l]
Concentration range (ppm)	0.2 – 60000	
Accuracy		5 mg/l [Cl-: 1 mg/l]
Temperature range	0 – 50°C	0 – 40°C
Diameter	12 mm	40 mm
pH range	3 – 10	4 – 11
Sensor type	PVC membrane	
Interfering ions	Cl–, Br–, NO2–	
Durability		4-8 Months
Comments		integrated temperature sensor

Specific literature:

{Radiometer analytical, ISE25S, “ MeterLab Guide to Reliable pH, Ion and Conductivity Measurements (Electrodes) Data Sheet (lit 4416)“, http://www.hach.com/fmmimghach?/CODE%3AL4416_01-0712747%7C1}

{WTW, http://www.wtw.com/media/OnlineMessKatalog2006_I.pdf [2007-09-07] p.38}

Azo Colouring Method (Photometric)

With this method nitrite concentrations can be measured intermittently on-line.

Functionality

By a reaction with nitrite a reagent produces a rose-pink colouring of the measuring solution. The colour intensity is proportional to the nitrite concentration in the sample and is measured with a two-jet reference photometer.

Practicability

Particularly for the application within the wastewater range, equipment from the company WTW is available. Its characteristic values are arranged briefly.

	WTW, TresCon ON 510
Concentration range (M)	0,40…90,0 µmol/l
Concentration range (ppm)	0,005…1,200 mg/l
Accuracy	0,1 µmol/l [0,001 mg/l]
Temperature range	
Diameter	
pH range	
Sensor type	Photometric,
Interfering ions	
Durability	½ year maintenance, calibration 24h,
Comments	The Device is analyzing samples taken in 10/15/20 min intervals. Cleaning-, calibration- and reagent-solutions have to be obtained.

Specific literature:

{WTW, http://www.wtw.com/media/OnlineMessKatalog2006_I.pdf [2007-09-07] p.45}

3.2.1.10 Conductivity

The electrical conductivity is a physical quantity, which indicates the ability of a material to conduct electric current. In aqueous solutions the conductivity as a sum-parameter is a measure for the ion concentration. The more salts, acids or also bases are dissociated, the higher the conductivity. The conductivity of wastewater can be easily measured to get information about possible dilution of wastewater with stormwater run-off.

Conductometric Analysis

Functionality

The measurement of conductivity is based on the principle of the electro-chemical resistance test. A measuring cell is used which consists of two similar electrodes. An alternating voltage is applied to the electrodes. From the current caused by the ions of the measured media, the conductivity value is computed. Cell geometry and the temperature influence the measured current and are considered throughout the computation [GRÜNDLER, 2003; HAMANN & VIELSTICH, 1985; DEV, 2003; RUMP, 2003].

Practicability

Conductivity sensors for the employment in wastewater are available from different manufacturers on the market. The most important characteristics are listed on two products.

Sensor	**Driesen&Kern, „µS-Log540“**	**WTW, TetraCon 700**
Measurement range	0,05…100ms Ranges: 0,05… 0,4 … 1,0 … 2,0… 3,8 … 7,9 … 100 mS	10µS/cm … 1000mS/cm Ranges: 0,0 … 0,2 … 2 … 20 … 200mS
Resolution	better than 0,1% upper limit of respective range	
Accuracy	better than 0,1% upper limit of respective range	
Allowed process pressure		0-10 bar
Temperature	Pt1000-Sensing resistor	NTC
Measurement range	0,2°C...+50°C	0 … 50°C
Resolution	± 0,1 °C	+/- 0,2K
Accuracy	± 0,2 °C	
Casing	V4A	PVC, V4A
Type of protection	IP68	IP68

Specific literature:

{http://www.driesen-kern.de/produkte/wasserseiten/loggerfuerdenunterwassereinsatz/01b6f9989a069a33b.html [2007-09-06]}

{WTW, http://www.wtw.com/media/OnlineMessKatalog2006_I.pdf [2007-09-07] S.26}

3.2.2 Measurement in Gas

3.2.2.1 Molecular Oxygen

Zirconium dioxide sensors

Zirconium oxide can be used for the measurement of concentration in gases.

Functionality

This electro-chemical measuring procedure is based on the oxygen conductivity of zirconium dioxide. The oxygen-containing measuring gas is conducted, for example, by a zirconium dioxide tube heated up to over 700 °C, which carries electrodes inside and outside and is exposed outside to the air. Thus, there is a development of electrical voltage at the electrodes, which depends, according to the Nernst-law, on the absolute electrode temperature and the relationship of the oxygen partial pressure at the two electrodes. The oxygen partial pressure of air serves here as comparison value [HAMANN & VIELSTICH, 1985; GRÜNDLER, 2003; RUMP, 2003; HÖLL, 2002; DEV, 2003].

Practicability

By zirconium dioxide sensors oxygen partial pressure within the ppm-range can be measured without problems. Preferential applications are flue gas measuring probes and the Lambda probes used in the motor vehicles.

Special designed devices can be used in the gas phase of sewers for the continuous measurement. The gas mixture must be sucked in by way of a hose and supplied to the measuring instrument. The characteristics of a measuring device are listed below. Other measuring devices are not known.

	Zirox, Module of oxygen detection ZR5
Measurement range	1 Vol.-ppm…100 Vol.-%
Accuracy	relative measuring error < 5 %
Detection limit	1 ppm, made-to-order item up to 10-15 ppm
Response time at 25 °C (Air –> N2)	t90 ≤ 1 s
Allowed process temperature	0…50 °C, max. 80 % rel. humidity
Comments	Ready to operate: < 15 min flow rate: 8 l/h ±2 l/h, controlled by internal pump

Specific literature:

{Co ZIROX GmbH, http://zirox.de/produkte/oem_loesungen/sauerstoffmessmodul_zr5.html}

Electro-Chemical Oxygen Sensor

The measurement principle of the electro-chemical cell is applied for the measurement of concentration of oxygen in gas mixtures. Different building methods are well-known, which differ according to the kind of the oxygen entrance to the measuring cell.

Functionality

All electrochemical oxygen sensors are of the self-powered, diffusion limited, metal-air battery type comprising an anode, electrolyte and an air cathode. An oxygen cell can simply be considered as an enclosure (either a metal can or a plastic moulding) which holds two electrodes: a flat PTFE tape coated with an active catalyst, the cathode and a block of lead metal, the anode. This enclosure is airtight apart from a small capillary at the top of the cell which allows oxygen access to the working electrode. The two electrodes are connected, via current collectors, to the pins which protrude externally and allow the sensor to be electronically connected to an instrument. The entire cell is filled with conductive electrolyte which allows transfer of ionic species between the electrodes. The rate at which oxygen can enter the cell is controlled by the size of the capillary hole at the top of the sensor. When oxygen reaches the working electrode, it is immediately reduced to hydroxyl ions:

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

These hydroxyl ions migrate through the electrolyte to the lead anode where they are involved in the oxidation of the metal to its corresponding oxide.

$2Pb + 4OH^- \rightarrow 2PbO + 2H_2O + 4e^-$

As the two processes above take place, a current is generated which can be measured externally by passing it through a known resistance and measuring the potential drop across it. Since the current produced is proportional to the rate at which these reactions occur, its measurement allows accurate determination of the oxygen concentration.

As the electro-chemical reaction results in the oxidation of the lead anode these sensors have a limited life. Once all the available lead has been oxidised they no longer work. Typically oxygen sensors have 1–2 year life time, however this can be lengthened by increasing the size of the anode or restricting the amount of oxygen that gets to the anode. {cp http://citytech.com/technology/02-sensors.asp [2007-09-06]}

Practicability

Electro-chemical gas sensors are susceptible against condensation. This requires, owing to circumstances, a complex preliminary drying of the two measured gas mixtures, which apparently react negatively on application in the wastewater pipe.

	CitiCel 2FO	**e2v technologies, EC 410**
Measurement range	0-25% Oxygen, max. 30%	0-30 %
Accuracy		0.1% O2
Detection limit		
Response time at 25 °C (Air –> N2)	t95 < 10 s	t90 < 15
Signal in Air		300 – 400 µA
Residual signal in O2-free medium		40 µA (in N2)
Allowed process pressure	Atmospheric ± 10%, Pressure coefficient: <0.02% signal/mBar	90 - 110 kPa (nominal) 0.07% typical signal per mbar change
Allowed process temperature	-20°C to +45°C Temperature Coefficient: 0.2% signal/°C	–20 to +55 °C Temperature Coefficient: <0.5% signal/°C
Frequency of necessary re-calibration		<2% change in output per month (long-term drift)
Durability	Two years in Air, Drift: <5% signal loss/year	>36 months
Comments	Operating Humidity: 0 to 99% RH non-condensing	15 - 95% RH (non-condensing)

Specific literature:

{ City Technology Ltd, http://www.de.citytech.com/PDF-Datasheets/2fo.pdf }

Fibre-optic Sensor

In the last decade a large number of measuring procedures have emerged from the range of fibre optics. Thereby, the absorption and fluorescence characteristics of materials are used in dependence of the light wave length as well as the change of refraction characteristics of the light conductor with accumulation of certain materials within ranges of the conductor.

For the measurement of oxygen, this principle of measurement can be applied both in the gas phase and for the measurement of liquids. For explanation of functionality see sec. 3.2.1.2. The practicability for measurements in the atmosphere of sewage pipes is not described.

3.2.2.2 Hydrogen Sulphide

Hydrogen sulphide (H_2S) is a badly smelling, poisonous gas. It is an extremely weak acid, whose salts are the sulphides. The concentration of hydrogen sulphide is to be determined in the gas area of the sewage drain. There are different measuring and sensor systems, by which some are still being investigated. The measurement principles are described below.

„Surface Chrominated Thick Film BST“

The measurement principle still is in research and can therefore only be described briefly. From literature it is well-known that different solid H_2S-sensors based on semiconductors metal oxides (SnO_2, ZrO_2, CeO_2, WO_3) were investigated. These can seize concentrations larger than 10ppm.

In the work mentioned here, a H_2S sensor is described and examined, its semi-conductor layer from $Ba_{(0.8)}$ $SR_{(0.2)}$ TiO_3 (short: BST) is manufactured in the screen printing method. The semi-conductor layer is improved additionally in the dipping procedure in an aqueous solution out of chromium trioxide (CrO_3). This increases the selectivity regarding the gas H_2S. The influence of this surface change was systematically examined and described in the work. It succeeded to develop a semi-conductor sensor, operated in the range the 0.1 to 20ppm. The optimal operating temperature sensor is with 350°C. The times for an answer are to 80% with 4 s and regeneration to 80% with 13 s.

Specific literature:

{„Surface Chrominated Thick Films of Ba(0.8)Sr(0.2)TiO3 for H2S Gas Sensing”, Authors: “G.H. Jain , L.A. Patil , P.P. Patil and U.P. Mulik”, in “sensors ISSN 1424-8220 © 2007 by MDPI” www.mdpi.org/sensors}

Infrared sensor

The absorption behaviour is used by radiation of a material for the determination of the concentration.

Functionality

The basic principles of operation of infrared gas sensors rely on the exploitation of the following facts:

A wide range of materials absorb infrared radiation (due to intramolecular vibrations). For any one material, the strength of absorption (absorbance) varies with wavelength (its absorption spectrum).Different materials have different absorption spectra.

This causes that certain basic components are common to all infrared gas sensors: an infrared source (e.g. incandescent lamp), a detector (e.g. thermopiles, pyroelectric detectors), a means to select appropriate wavelengths (e.g. band pass interference filter) and a sample cell. Radiation from the source passes through the sample cell and wavelength selector. The choice of wavelength has a large bearing on the relative selectivity of the sensor. The radiation NOT absorbed by the sample is then detected and the ratio of this to the incident provides a measure of the concentration of target gas in the sample. A second detector (or channel) tuned to a different wavelength that is not attenuated by any species likely to be present in the sample is normally used to provide this reference measurement.

A further component that enhances the performance of IR gas sensors is a temperature sensor. All these components have temperature dependencies which must be compensated to provide an accurate measure of gas concentration. This temperature sensor (typically a thermistor) should be sited within, or in very close proximity to, the detector(s).

Infrared sensors effectively give a measure of the number of target gas molecules in the light path between source and detector. Consequently, the output signal not only varies with concentration but also barometric pressure i.e. they are partial pressure devices. For very high measurement accuracy, compensation for barometric pressure is, therefore, required. This dependency also infers that sensors with longer optical path lengths (i.e. distance travelled by radiation between source and detector(s)) will have increased sensitivity and tend to have a lower dynamic range but increased resolution.

In a single target gas, fixed optical light path device under constant barometric pressure, the signal output (and signal/noise ratio) approximately exponentially decays with increasing concentration i.e. infrared gas sensors are inherently non-linear. The measurement accuracy decreases with increasing concentration.

The components described above form a typical infrared gas sensor. However, some supporting electronics is required in any practical system. The more common detector technologies provide very small analogue signal outputs that require amplification. Basic analogue filtering of the amplified output signal can then enhance measurement accuracy.

The source also requires a driver circuit. It is usual practice to modulate the source output by pulsing (although some older design used fixed illumination and mechanical choppers). This creates periodic variations in the emitted intensity and so allows the use of synchronous detection techniques.

To carry out the temperature and barometric compensations, it is common practice to use computational algorithms inside a microprocessor. This first requires the analogue signals to be converted into digital signals. The compensated data is then transmitted to the user in some form.

{cp http://citytech.com/technology/irsensors.asp [2007-09-06]}

Practicability

There is no information available, whether this principle can be applied to measure in the gas phase of sewer networks.

Pellistor

Functionality

Pellistors employ catalytic combustion to measure combustible gases or vapours in air up to the Lower Explosive Limit (LEL) of the gas.

The standard sensor consists of a matched pair of elements, typically referred to as a detector and compensator (reference element). The detector comprises a platinum wire coil embedded within a bead of catalytic material. The compensator is similar except that the bead does not contain catalytic material and as a consequence is inert.

Both elements are normally operated in a Wheatstone bridge circuit that will produce an output only if the resistance of the detector differs from that of the compensator.

The bridge is supplied with a constant dc voltage that heats the elements to 500-550°C. Combustible gases are oxidised only on the detector element, where the heat generated increases its resistance, producing a signal proportional to the concentration of combustible gas. The compensator helps to compensate for changes in ambient temperature, pressure, and humidity, which affect both elements equally.

Most pellistors have the pairs of elements housed in separate metal cans. In a complete gas detector (to be used in a potentially explosive atmosphere) the cans will normally be mounted inside a flameproof enclosure consisting of a metal sinter and housing. This enclosure allows gas to reach the sensor whilst ensuring that the hot sensor elements cannot ignite an explosive gas mixture. As an alternative complete detectors are available with both elements mounted inside a flameproof enclosure approved to the latest European (ATEX) and North American (CSA & UL) standards.

Detection of explosive atmospheres relies on the accurate measurement of combustible gases below the LEL concentration. Safety applications, therefore, are not generally concerned with measuring the volume concentration of gas. Measurements are more usually expressed as a percentage of the LEL concentration of the gas (%LEL).

Most combustible gas detection techniques are designed to detect a wide range of gases. Ideally the output of a sensor will be independent of the gas being measured. In reality, however, the variation in physical properties affects the output. Catalytic oxidation sensors are no exception, so the response a pellistor gives to the same volume concentration of different gases will vary. However when exposed to the same %LEL concentration of different gases, the variation in output is fairly small compared to other detection techniques. As safety applications are interested only in %LEL measurements this is a major advantage.

The variation in output for the same %LEL concentration of different gases is termed ‘relative sensitivity’.

Practicability

There are effects which limit the application framework of these sensors. The two most important are outlined briefly:

Poisoning

Some compounds will decompose on the catalyst and form a solid barrier over the catalyst surface. This action is cumulative and prolonged exposure will result in an irreversible decrease in sensitivity. Typical poisons are organic lead and silicon compounds.

Inhibition

Certain other compounds, especially halogenated hydrocarbons, are absorbed or form compounds that are absorbed by the catalyst. This absorption is so strong that reaction sites in the catalyst can become blocked and normal reactions are inhibited. The resultant loss of sensitivity is temporary and in most cases a sensor will recover after a period of operation in clean air.

Pellistors are available for the measurement of H_2S on the market. The behaviour of the sensors depends nonlinearly on concentration, the sensor and the circuit, in which it is operated. On their behalf, important characteristics for a specific sensor head are arranged below.

	e2v technologies, VQ101
Operation	continuous
Stabilisation time	1 h
Power supply	6.5V +/- 1.5V
Sensor current consumption	400 mA max.
Output in clean air	500…700mV
Response in 10ppm hydrogen sulphide	90…225mV
Deviation of response at 5ppm	+/-25mV
Deviation of response at 25ppm	+/-25mV
Life time	many years

Specific literature:

{ e2v technologies, http://www.e2v.com/files/sensors/vq101.pdf }

{cp http://citytech.com/technology/pellistors.asp [2007-09-06]}

Electro-chemical

The general electro-chemical measurement principle was already described for the oxygen measurement [sec. 3.2.2.1]. It is dealt with more deeply here but with only with the characteristics for the measurement of H_2S.

Functionality

Electrochemical toxic gas sensors are micro fuel cells. They have a direct response to volume concentration of gas rather than partial pressure.

The simplest form of electrochemical toxic sensor comprises two electrodes: sensing and counter, separated by a thin layer of electrolyte. This is enclosed in a plastic housing that has a small capillary to allow gas entry to the sensing electrode and includes pins which are electrically attached to both electrodes and allow easy external interface. These pins may be connected to a simple resistor circuit that allows the voltage drop resulting from any current flow to be measured. Gas diffusing into the sensor is either oxidised or reduced at the sensing electrode and, coupled with a corresponding (but converse) counter reaction at the other electrode, a current is generated through the external circuit. Since the rate of gas entry into the sensor is controlled by the capillary diffusion barrier, the current generated is proportional to the concentration of gas present outside the sensor and gives a direct measure of the toxic gas present.

The central feature of the design is the gaseous diffusion barrier, which limits the flow of gas to the sensing electrode. The electrode is therefore able to react with all target gas as it reaches its surface, and still has electrochemical activity in reserve.

From the reaction at the counter electrode, it is evident that oxygen is required for the current generation process to take place. This is usually provided in the sample stream by air diffusing to the front of the sensor, or by diffusion through the sides of the sensor (a few thousand ppm is normally sufficient). However, continuous exposure to an anaerobic sample gas may result in signal drift, despite the oxygen access paths and so it is recommend that toxic sensors are never potted with resin or completely immersed in an anaerobic gas mixture.

For certain demanding applications where the sensors are frequently exposed to very high concentrations of the analyte, for example in flue gas analysis, it may be necessary to ensure there is an additional source of oxygen access to the counter electrode.

2-electrode sensors are the simplest form of toxic gas sensors. However they have limited measuring range due to polarisation of the counter electrode. This polarisation effect can be eliminated by using a third, reference, electrode with a stable potential in the sensor design. In these sensors the sensing electrode is held at a fixed potential relative to the reference electrode (from which no current is drawn) so both maintain a constant potential. The counter electrode is still free to polarise, but has no effect on the sensing electrode and does not limit the sensor in any way.

3-electrode sensors are the most widely used design of electrochemical sensors for detecting toxic gases. Despite this there are some applications where the 3-electrode design proves inadequate. For example cross-interfering gases or zero-offset changes with temperature can compromise their overall performance. By introducing a fourth ‘auxiliary’ sensor accurate sensor performance can be maintained while also allowing the simultaneous measurement of two gases.

A 4th auxiliary electrode can assist in overcoming cross interference from other gases. The main sensor is responding to the desired gas while the auxiliary electrode is responding to the interfering gas alone. Once the ratio of the responses on each electrode is known, a compensated signal can be obtained by subtracting the auxiliary signal from the sensing electrode signal with an analogue circuit or using a microprocessor with appropriate software.

The baseline signal of most electrochemical sensors tends to increase exponentially with temperature, approximately doubling for every 10°C rise in temperature. For the majority of applications this does not normally present problems but for applications involving very low concentrations of gases any baseline shift with temperature could seriously affect the ability to measure these gases accurately. The signals from both the sensing electrode and auxiliary electrode will both show similar responses to changes in temperature but because the auxiliary electrode is not exposed to reactive gas, its signal can

simply be subtracted from that of sensing electrode. This is a useful method of compensating for any baseline shifts that would normally occur as a result of changes in temperature, but is not ideal.
{cp http://citytech.com/technology/toxic-sensors.asp [2007-09-06]}

Practicability
Electro-chemically working sensor measuring heads and sensors are available on the market. The characteristics for a sensor head are indicated below.

	City Technology, H2S 3E 100 S Amperometric 3 electrode sensor cell
Operation	continuous
Life time	> 48 months
Measuring Range	0-100ppm
Sensitivity Range	750 nA/ppm ± 150 nA/ ppm
Zero Current at 20°C	< ± 200 nA
Resolution at 20°C	< 0.3 ppm
Bias Potential	0 mV
Linearity	< 5% full scale
Response Time at 20°C	t50 < 15s, t90 < 30s
Long Term Sensitivity Drift	< 10% per 6 months
Humidity Range	15–90% r.H., non–condensing Effect of Humidity: < 1 ppm at abrupt changes of humidity

Specific literature:
{City Technology Ltd., http://citytech.com/PDF-Datasheets/h2s3e100s.pdf [2007-09-06]}

3.2.2.3 Organic Solvents

The term “organic solvents” comprises a multitude of different substances. They are both present in wastewater and the gas area. As a result of its inhomogeneous distribution and transport behaviour in wastewater the measurement in the gas phase is to be made. There is no information known about sensors, which can measure the concentration of this group of substances online. It would be therefore appropriate to determine this group of substances with the sum parameter VOC (volatile organic compounds). Electronic noses could also be applied. No sensors exist for the measurement of VOC. The analysis is complex using special devices, usually gas chromatographs

Flame ionization detector (FID)

Functionality

The operational principle is the measurement of the conductivity of a oxyhydrogen gas flame (gaseous fuel is hydrogen) between two electrodes. Substances which are to be analyzed are transported with a feed gas stream into the flame and ionized there, thermally. The electrons that are set free with the ionization are captured and noted as a peak by an attached writer or a data system. An FID is more sensitive up to 1000x than the heat conductivity detector. Furthermore, the detector signal is linear proportional over a wide concentration range to the quantity of the carbon content of the analyte. Therefore, the concentration of a hydrocarbon can be derived from the signal without calibration, so that the detector can be applied well for quantification [GRÜNDLER, 2003, DRESSLER, 1986].

Practicability

The most frequently applied detector in the gas chromatography is the FID, since it connects robustness with high sensitivity. An FID is more sensitive up to 1000x than the heat conductivity detector. The maintenance is extensive because of the supply of pure detonating gas (H_2), which has to be re-filled every few days.

Different manufacturers offer devices with FID-principle for measurement. Different examples with characteristic values of equipment are mentioned below.

	Environnement S.A, Graphite 730
Ranges	0-10/0-100/0-1000/0-10000 ppm
Accuracy	1% of full scale
Response time	< 3sec
Zero drift	< 1% / 7d
Span drift	< 1% / 7d
Temperature of heated block	180°C
Operating temperatures	5 – 45°C
Autonomy	50 h with a B1 cylinder of H2/He at 150 bar
Scan frequency	20sec

Specific literature: { Environnement S.A, http://www.environnement-sa.com/index2.html }

Photoionization Detector

Functionality

A photoionization detector or PID uses an ultraviolet (UV) light source to break molecules to positively charged ions that can easily be counted with a detector. Ionization occurs when a molecule absorbs high energy UV light, which excites the molecule, and results in temporary loss of a negatively charged electron and the formation of positively charged ion. The gas becomes electrically charged.

In the PID, the charged particles produce a current that is amplified and measured. This current correlates to the amount of particles in the analyte.

{cp http://en.wikipedia.org/wiki/Photo_Ionization_Detector }

Practicability

Different manufacturers offer devices of this principle. The PID as well as the FID just gives a response according to the **sum** of VOCs. For identification and quantification of distinct solvents, a separation of the gas mixture using gas chromatography is necessary.

Specific literature:

{Ama Instruments Gmbh, Produktinformation GC 5000 Process, http://www.ama-instruments.com

Infrared sensor

The absorption behaviour is used by radiation of a material for the determination of the concentration.

Functionality

See description above within the sec. 3.2.2.2.

Practicability

There is no information available, whether this principle can be applied for measure in the gas phase of sewer networks.

3.2.2.4 Odour measurement with electronic nose

An electronic nose is a technical system for the measurement of odours. For this purpose microelectronic gas sensors produce electronic signals. The term electronic nose unites „recognising “of smells with the technical implementation by electronic sensors. It is to be noted that there cannot be an electronic nose in the technical sense, since odours must be interpreted by the brain. Technical measuring systems in contrast supply data about gas concentrations, of non-smelling as well as smell-active gases.

A typical electronic nose consists of a number of gas sensors, whose signals are processed by mathematical methods in the sense of pattern recognition. In practice abstract mathematical methods, for instance the main component analysis, are applied. Thereby the pattern information is projected onto a two-dimensional plane, on which similar patterns overlap the same regions.

A number of different technical sensors are used in electronic noses. The main ones are:

- Sensors on basis of semi-conducting metallic oxides, abbr. MOS sensors.
- Sensors with electrically conducting polymers. There are independently (intrinsic) conducting polymers and such, with a conducting component, such as graphite, added.
- Sensors, evaluating mass effects, with the two groups of swinging quartz sensors (QMB/QCM sensors) and the surface wave sensors (SAW sensors).

Each of these sensor types has its own instrumental characteristic. In particular, the chemical range measuring of gases differ. MOS sensors preferably measure low-molecular oxidizable gases. With conducting polymers polar gas components are well measured, mass-sensitive sensors measure high-molecular materials preferentially. In technical application however, in particular the measuring stability of the sensors is a crucial parameter during longer periods, since they must hold the calibration information. Depending upon the principle of operation of the sensors and their specific application, hence, measures must be planned for the protection and verification of the sensors.

The gas sensors used in electronic noses are often constructed in the form of specially grouped gas sensors partially mounted on a microchip. One speaks here of sensor arrays or chemo sensor arrays.

[FRECHEN, 2007; {cp http://de.wikipedia.org/wiki/Elektronische_Nase}]

Sensor-Array with Temperature Gradient (MOS)

Functionality

The sensors exhibit, depending on the operating temperature, for each gas another specific affinity/detection rate. This is utilised when measurements are taken with the same sensors at the same time at different temperatures. After applying a complex data analysis the components in the gas mixture and their concentrations can be reconstructed.

Practicability

The measurement can only be successfully accomplished for a limited number of components in the gas mixture. If unknown compositions with more than 5 components are involved, no meaningful statements about their concentrations can be derived.

The requirements in the wastewater pipe with its complex and unknown gas mixtures cannot be fulfilled by these devices. Therefore further adjustments have to be carried out.

A piece of equipment lies in the range of 20.000 €. In the following table the specifications of the product Artinos are listed.

Specification	
Substrate	Si/SiO2 or Al2O3
Gas detecting layer	SnO2 or WO3
Gradient membrane	SiO2
Sensor segments	38 or 16
Size	9x10 mm² (38 Seg.) or 3x4 mm² (16 Seg.)
Temperature sensor	2 heating elements: 4
Average operating temperature	200 - 400°C
Consumption at 300°C in stationary air	ca. 1 Watt (16 Seg., hanging in ceramic card)
	ca. 6 Watt (38 Seg., on bearings in PGA-socket

Selection of detection limits at standard environmental conditions	
Ozone, NH3, H2S, Xylol, Acrolein, Ethanol, Methanol, Acetone, Ethylaceton, Toluol, DMF...	< 100 vppb
Methan, Propan, NO2, SO2, Benzol, CO ...	< 1 vppm
CCl4, CHCl3, C2HCl3 ...	< 100 vppm

Specific literature:

{Interview with Co Sysca über Artinos[2007-05-00]}

{http://sysca-ag.de/ product: Artinos}

Mass sensitive Swinging Quartz-technology

Functionality

Core elements are several sensitive gas sensors, which work on the basis of mass sensitive swinging quartz technology. In a sensitive layer coating a swinging quartz (10 million oscillations per second) gases and odours are stored. Thus, the mass of the layer changes and consequently the resonant frequency of the swinging quartz is adjusting. Such alteration is the measuring signal. The storage of gases corresponds to a dissolving process. When the gas is no longer present in the environment of the quartz, the absorbed molecules leave the layer and the sensor returns to its neutral signal. The measurement can be improved through a gas enrichment by thermal desorption. A partial separation of gases according to the responding sensor increases the sensitivity, likewise. The applied algorithms in pattern processing are crucial for the evaluation [GRÜNDLER, 2003; http://www.sysca-ag.de/artinos.htm].

Practicability

A system manufactured by the company AltraSens (OdourVector) is used in practice for the monitoring of different processes. It consists of 6 sensors, which prefer high-molecular substances with offensive smells.

According to the manufacturer, odour emissions from the sewer system were measured. Likewise, a biological clarification plant in a long-term monitoring was accompanied.

Specific literature: {Co Altrasens, http://www.altrasens.de}

3.2.3 Measurement in Biofilm

3.2.3.1 pH-value

Principle of measurement and functionality are the same like in wastewater (see sec. 3.2.1.1).

Galvanometric pH-Meter

Practicability

For the pH measurement in semi-solid materials, for example in the area of the food industry (measurement in meat, sausage and cheese) are puncture-pH-probes for measurements available. These matrices contain bio molecules, as to be expected in biofilms and in addition triglycerides (fats) and higher protein levels that make pH-value measurements difficult. Therefore, application appears to be possible for pH-determination in biofilm with these sensors. However, no experience exists for continuous use and application in sewage area with these electrodes.

	Hebesberger Mess- & Regelgeräte
Measurement area	1...14 pH
Accuracy	0,02 pH
Allowed process temperature	-10°C...+50°C
Comments	Data logger with its own autonomous battery conceived for use in waters. Pt-Temperature measurements and automatic compensation BNC input jack

Specific Literature: { www. hebesberger. at }

Thick Film pH-Sensor

Practicability

The ranges of application, for the sensor, are the chemical industry, food technology and medical technology. Because of its design without fluid contact to a damageable glass membrane, its use in the biofilm or even in the condensing atmosphere of sewage might be theoretically possible. Anyhow, such an application is without description and must be exactly examined. A commercial manufacturer is not known.

	Thick Film pH Sensor
Measurement range	1…9 pH
Accuracy	0,3 pH
Speed of response	< 1s
Allowed process temperature	25 – 55 °C
Comments	drift < 2mV/d (<0,04 pH/d), drift reference electrode < 1mV/d

Specific literature:

{Fraunhofer Institut Keramische Technologien und Systeme, Informationsblatt Thick Film pH Sensor, Messestand Sensor+Test, Nürnberg 2007}

3.2.3.2 Determination of biofilm activity

Intensive research in measuring methods for biofilms has been done in the last years. A set of measurement principles for application on the biofilm were developed. All information is taken from the surrounding fields of research. None of these measurement principles are commercially available yet. The methods are described below.

Optical Sensor

A sensor has been developed which examines the characteristics of the biofilm with photometric methods.

Functionality

Transmission, dispersion and fluorescence are measured continuously by the sensor. The measuring procedure is accomplished in a flashing operational mode of the sensor. The dark signal is measured in the dark phase between two pulses. Parallel to it a reference signal is measured for the characterization of the linked radiation intensities. Each measured value is corrected concerning dark signal and standardized on the reference signal. The transmission, dispersion and fluorescence are measured with 3 different UV-wavelengths and a NIR-wavelength. The measured optical values are correlated with the biofilm thickness and the number of cells. The characteristics of the biofilm are thus determined

Practicability

The dynamic behaviour of the different optical parameters in view of the processes in the biofilm has not yet been sufficiently examined. Precise mathematical-empirical methods and algorithms for statements about biofilm need to be developed. It is expected that by the sensor detailed process characteristics and biochemical parameters can be measured.

Specific literature:

{KWB Band 4, Mittenzwey, Szewzyk, Dworak & Schulze „Online-Sensor zur Erfassung von Biofilmen“, Berlin 2006}

Ultrasonic Scan

There are studies investigating the application of the procedure of high frequency ultrasound measurement to biofilms. The advantage of this procedure is the production of three-dimensional in situ pictures of a biofilm sector, which hopefully allows for an exact analysis of the structure and the development of the biofilm.

The research in this area is still in a very early stage and an application in the laboratory for the biofilm of a species was examined.

Specific literature:

{http://www.ncbi.nlm.nih.gov/sites/entrez?tmpl=NoSidebarfile&db=PubMed&cmd=Retrieve&list_uids=17604896&dopt=AbstractPlus}

1 Electro-chemical

Functionality

Two metallic electrodes which are isolated from each other are provided over an energy source with a potential difference from 50 to 500 mVs. Due to the potential induced depolarization-effects a flowing direct current through the biofilm is measured. Likewise, the current conduction, which flows after switching the energy source off, is measured, as well as the electrical resistance between the electrodes which characterizes mainly the biofilm.

Practicability

The application of the sensor in wastewater is not clarified. A manufacturer was not found.

Specific literature: {Source: US Patent 5,356,521 - 18th October 1994}

2 Optical Coherence Tomography

Functionality

Optical coherence tomography (OCT) is an interferometric, non-invasive optical tomographic imaging technique offering millimetre penetration (approximately 2-3 mm in tissue) with micrometer-scale axial and lateral resolution.

OCT is based on low-coherence interferometry. In conventional interferometry with long coherence length (laser interferometry), interference of light occurs over a distance of meters. In OCT, this interference is shortened to a distance of micrometres, thanks to the use of broadband light sources (sources that can emit light over a broad range of frequencies). Light with broad bandwidths can be generated by using superluminescent diodes (superbright LEDs) or lasers with extremely short pulses (femtosecond lasers). White light is also a broadband source with lower powers.

Light in an OCT system is broken into two arms, a sample arm (containing the item of interest) and a reference arm (usually a mirror). The combination of reflected light from the sample arm and reference light from the reference arm gives rise to an interference pattern, but only if light from both arms have travelled the "same" optical distance ("same" meaning a difference of less than a coherence length). By scanning the mirror in the reference arm, a reflectivity profile of the sample can be obtained (this is time domain OCT). Areas of the sample that reflect back a lot of light will create greater interference than areas that don't. Any light that is outside the short coherence length will not interfere. This reflectivity profile, called an A-scan contains information about the spatial dimensions and location of structures within the item of interest. A cross-sectional tomograph (B-scan) may be achieved by laterally combining a series of these axial depth scans (A-scan). En face imaging (C-scan) at an acquired depth is possible depending on the imaging engine used.

Practicability

The procedure of the OCT was applied in the laboratory at TU-Munich for none-invasive measurement of biofilms in the pipe. Growth and also peel off processes could be recorded on-line. It was possible to record the processes in a temporal resolution within the range of seconds to minutes. The authors express hope that the procedure will be established as a standard technique for the monitoring of biofilms.

Specific literature:

Meier, Optical Coherence Tomography, Technische Information, Berner Fachhochschule Technik und Informatik

{cp http://en.wikipedia.org/wiki/Optical_coherence_tomography [2007-09-06]}

{"Visualisation of transient processes in biofilms by optical coherence tomography.", Haisch C, Niessner R.,Water Research 2007 Jun;41(11):S. 2467-72. Epub 2007 Apr 25.}

3.2.4 Measurement in Material (Reinforced Concrete)

Sensor for early detection of corrosion in concrete structures

Steel-reinforced concrete structures such as sewer pipes, cooling towers or rock anchors are often exposed to a wide variety of damaging influences. Aside from mechanical stress, corrosion of steel is one of the most relevant damaging processes in steel-reinforced concrete. It presents a safety risk to people and environment because failure can occur without prior indication. Besides moisture and chloride ions concentration, pH-value is a chemical parameter of major importance in health monitoring of steel-reinforced and pre-stressed concrete structures. The lifetime of steel-reinforced concrete structures depends strongly on their pH state as embedded steels in concrete structures are only passivated at pH-values higher than about 9. For this reason, long-term monitoring of pH-value in the range from 9 to 13 with a resolution of about 0.5 pH units is relevant for early detection of potential corrosion condition.

Commercially available structure-integrated sensors for early detection of steel corrosion in concrete structures do not always sufficiently match the in-situ requirements. Fibre optic based sensors are a promising technology for corrosion monitoring because they offer a large number of attractive features such as small size, flexibility, geometric versatility, resistance in corrosive and hazardous environments, no signal interference due to present moisture, in-situ and non-destructive measurement, and immunity against lightning strokes. In order to draw benefit from these advantages, a concrete-embeddable long-term stable fibre optic pH sensor was developed. The most challenging requirements concern the long-term stability under strong alkaline conditions within the pH range between 13 and 9 over a period of at least 25 years. The sensor has to be integrated in harsh environments and inaccessible places. It must be guaranteed that the sensing element has an intimate contact to the concrete matrix to see pH changes. And finally, the price of pH sensors has to be as low as possible to enable the fabrication of multiple-sensor structures.

The fibre optic pH sensor consists of a pH-sensitive layer made of a pH indicator immobilized in a solid substrate. As a result of intense investigations, the absorption method was preferred because only this method provided reliable measurement results. In order to overcome instability problems resulting from decrease of the indicator concentration due to photodegradation or leaching out, drifts of the light source intensity or bending of optical fibres, a ratiometric method based on the use of the ratio between the intensity at two different wavelengths (e.g. at the intensity maximum points or at the isosbestic point) was applied. Such a ratio of intensities is not altered by external factors. The measurement principle and some more details are described in DANTAN et al. (2005).

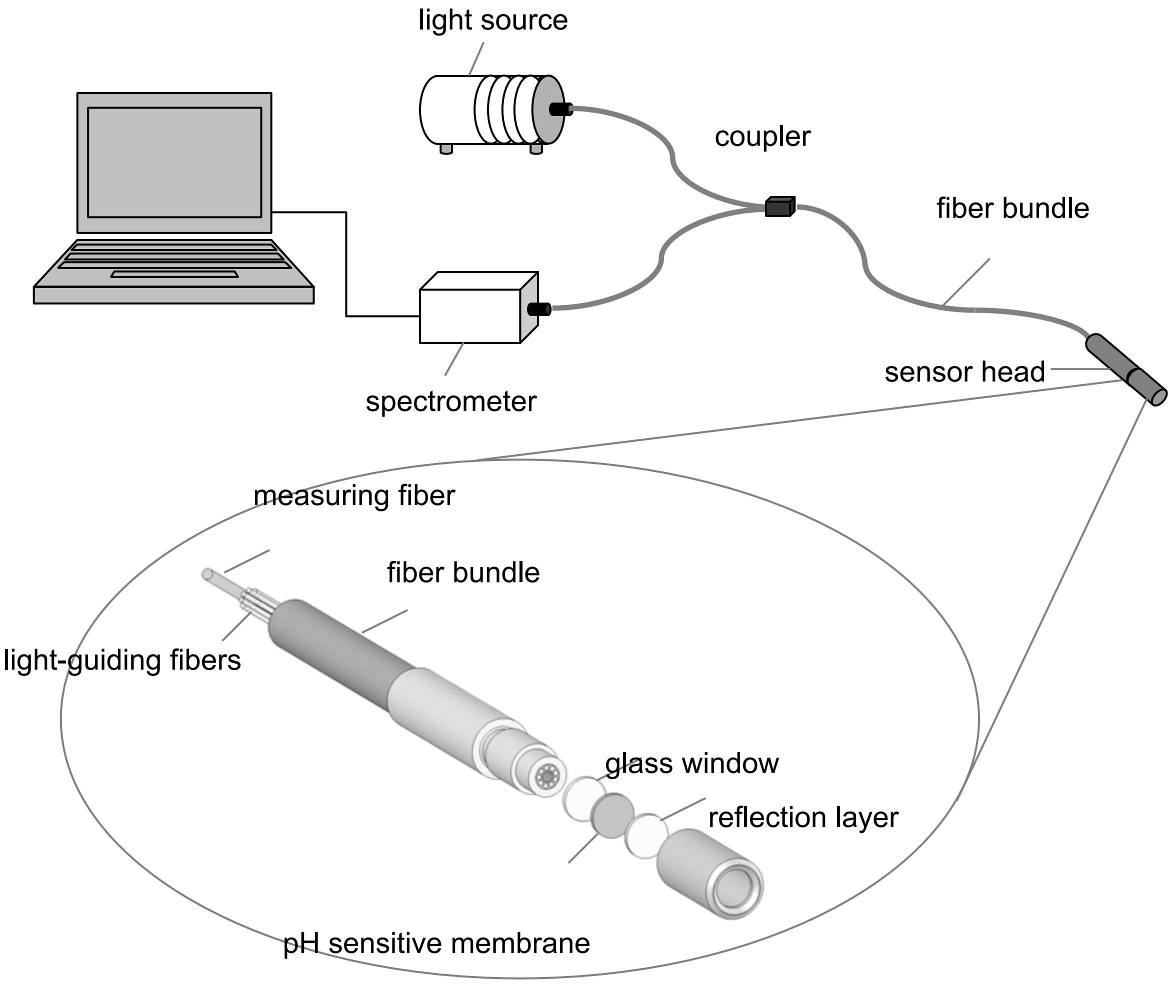


Figure 9: INSTRUMENTAL SETUP FOR PH SENSING BASED ON ABSORPTION METHOD, AND EXPLODED VIEW OF THE SENSOR HEAD (FROM DATAN)

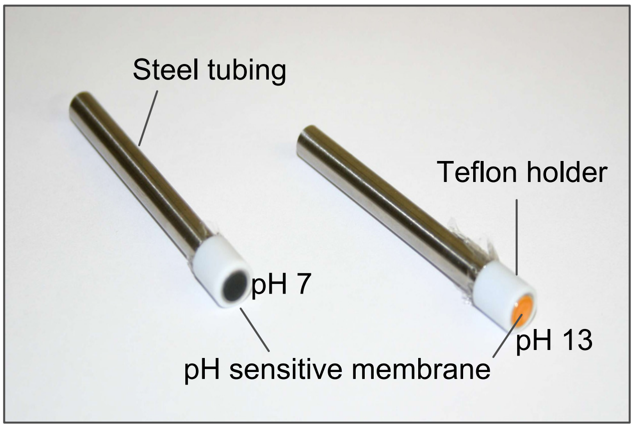


Figure 10: PH SENSOR HEAD DESIGN; THE HEAD IS PLUGGABLE AND CAN BE REPLACED. PHOTO: BAM

The diameter is 8 mm; the sensitive layer is protected but sufficiently sensitive for contact to the concrete matrix. The sensitive membrane must not exceed a definite thickness because the ion diffusion is hindered. In order to ensure a reliably stable thickness of the sensitive membrane, a special powder compacting tool for manufacturing of pH-sensitive membranes was developed.

The measurement resolution of the sensor for pH-values between 9 and 12 is in the range from 0.1 to 0.6 pH units depending on the pH-value. The highest resolution can be achieved in the middle of the measurement range (between 9.7 and 11). One particular condition of use is that the pH sensitive membrane must not dry out. This requirement is mostly fulfilled in hydraulic engineering and geotechnical applications. In order to prevent drying out before integration into concrete structures, the pH sensitive membrane must be protected by a small watertight topcoat.

Figure 11: Prefabricated anchors with fixed pH sensors (arrows). Photo: BAM

Figure 12: Water filled topcoat for the pH-sensitive membrane to prevent dehydration. Photo: STUMP GmbH

Suitability of this sensor has been tested in steel anchors installed in the harbour of Rostock (North Germany). Fig. 18 shows two of totally 10 pH sensor prototypes that have been fixed on prefabricated anchor bodies (two in each anchor) before introducing them into the borehole. The topcoat (Fig. 17) was removed shortly before introducing the anchor into the borehole and concreting it. This procedure ensured that the membrane maintained its hydrophilic properties. Since sensor installation in July 2005, seven of 10 installed sensors have provided useful information about the pH-value of the grout. (Two sensors were damaged already during installing the anchors, one sensor failed after few months.)

The sensor concept has been prepared for commercial supply. Relating to his, special attention was put on optimization of the robustness of the sensor components and integration technology. A series of investigations have been carried out to clarify whether the membranes are reliably capable of recording pH changes in concrete structures. For this purpose, several sensor heads were embedded in fresh mortar test prisms according to the standardized testing procedures[6]. After a one-month curing period in water, the mortar samples with integrated sensor heads have been stored in an acid bath for simulation of pH decrease. The sensor signal has been monitored periodically and showed expected pH changes of the concrete matrix. Currently, the transfer of the research results into production will be arranged by the research partners of the German research project: BAM Berlin, Schmidt & Haensch GmbH Berlin, MBF GmbH Berlin (MPA Berlin Brandenburg) and Dietz Geotechnik Consult Hilden.

3.3 Abstract and Demands for Research & Development Sensors

The investigation on existing sensors in relation to the necessary parameters to be measured, determining the condition of technical wastewater facilities, regarding the presence of odour and corrosion effective substances, results in the following:

Plastic corrosion (aromatic and halogenated hydrocarbons)

Sensory processes for the continuous monitoring of concentration of halogenated and aromatic hydrocarbons in sewage do not exist.

For detection in the headspace, there are a number of procedures, but they merely permit a summarizing measurement of organic compounds in the gas. Of all of the described methods, the IR-sensor shows the highest selectivity (detection of CH-binding). The sensors are in fact specified for measurements up to 100% rel. humidity. Experience on a continuous application in the headspace of wastewater facilities do not exist.

No sensory processes exist for continuous surveillance of biofilms.

Concrete corrosion (sulphuric acid)

There are no proven methods for continuous sensory determination of pH-values and concentration of sulphate in biofilm.

In particular, the development of sensors for continuous monitoring of pH-values in biofilm of the headspace would be highly relevant for the early detection of possible damage in wastewater facilities through dissolving concrete corrosion.

There is a functioning prototype of a fibre optic sensor for the sensory detection of pH-value in reinforced concrete of wastewater facilities currently in development with the participation of the MPA Berlin-Brandenburg. The system is within the scope of a further research project, currently being tested.

Measurement of H_2S for Odour

For the H_2S-measurement in the headspace, different measurement principles are established. For example, electrochemical sensors or infrared sensors for measurements over a shorter period are in practice since years. Tests for endurance have to be carried out for long-term continuous measurement of H_2S in the headspace of wastewater facilities.

Additional parameters for modelling (simulation system)

For the determination of additional parameters that are important for the acquisition and modelling of chemical and biological relationships (see introduction, sec. 3.1) only sensors for continuous determination of oxygen concentration in the wastewater exist and are used in the practice.

For continuous determination of sulphate-content in wastewater, sensors do not exist. For the continuous determination of sulphide-content in wastewater, the existing sensors show low long-time stabilities and high-cross sensitivities. Here are just analyzers available that take virtually continual probes from the wastewater stream and carry out automated analysis.

For all other parameters (for example, organic sulphur compounds, COD, BOD in wastewater), there are also only laboratory procedures or expensive virtually continual procedures where sewage is extracted and analyzed in accordance to laboratory procedures. The organic load, determined by COD and BOD can be correlated to UV-absorption to some extent (see sec. 3.2.1.4). But anyhow, they need calibration against COD and BOD of a specific sewage.

The procedures for determining biological activity of biofilms are in the development stage. It is not clear whether the measurement of biofilm activity is sufficiently specific enough to deliver relevant information on the problems of odour and corrosion.

On the other hand, the measurement of physical parameters (relative humidity, temperature, air pressure and flow rate), are no problem.

The following table reflects the Table 6 in sec. 3.1, supplemented by information about sensors that exist for the measurement of major odour-active and corrosion-active substances for plastics and concrete, also for the measurement of substances involved in the formation of these matters, depending on their resources (wastewater, gas, biofilm, pipe material).

Table 8: Corrosive compounds, their causing parameters, precursors and reaction product, importance to measure and existing sensors

Corrosive Compound	Sewage	Gas	Biofilm	Material
Plastics				
Org. Solvents	+	++	0	
Desirable to measure	+	++	-	
Existing sensors	-	+	-	
Concrete				
Sulphuric acid: (H_2SO_4)	O_2, org. sulphuric com-pounds, SO_4^{2-}, HS^-, S^{2-}	H_2S (Odour)	acid (H_3O^+), (SO_4^{2-}), bioactivity	Gypsum, pH-value
Desirable to measure	+ (O_2, $SO_4^{2-}S^{2-}$)	++	++ (acid) + (SO_4^{2-})	+ (pH-value)
Existing sensors	+ (O_2), - (SO_4^{2-}), -+ (S^{2-})	+	- (acid), - (SO_4^{2-})	0 (proto-type)

Chapter 4

Data processing

The application of a numerical prediction tool to a real sewage system requires a model of this sewer system. In such a model, temporal-immutable properties, such as the course of sewage segments, their length, height or slope, pipe diameter, channel types, intakes or public sewers have to be included. The utilized materials are assigned to various segments. Furthermore, time-varying quantities in the simulation domain are necessary. They are provided as initial and boundary conditions for the simulation. Time-varying variables include all sensory and analytically measured quantities. The parameters controlling the operation of a sewage network have to be included, as well. The time-varying boundary conditions for the simulation up to the current moment are conveyed of historic measurement data of each sewer segment. For the forecasted periods the boundary conditions of historical data will be extrapolated or plausibly assumed.

The task of data processing for a pilot plant is to ensure the full and complete documentation of the long-term experiments for a number of years. For this reason an extensive data base is arising. Out of this data base the necessary input parameters are compiled, so that the simulations of the processes in sewage pipes are made possible. For the planned development of hydrodynamic model concepts, a calibration and validation is essential. For this purpose, recorded measuring data stored in the data base will be used. For analysis of various hydrodynamic model variations, it is necessary to compare and evaluate model results with each other. These comparisons are to be documented for research progress in the numerical simulation and hence, should be stored in the data base.

The transfer of available techniques for the present task has not yet taken place. Solutions are available for the individual parts linked with the data management for the planned pilot plant. The implemented work is therefore geared to the application of available concepts and strategies for the necessary data management. Essential tasks in this context are described below.

4.1 Structure of the data base

Over the entire period in the operation of a pilot plant, data must be recorded in the data base. The incoming data is being collected for this reason. There are different types of accumulated data that need to be considered here.

In the area of sensors continuous measured data in an electronic form will be expected. Which interface is used depends exactly on the sensors and their technical connections.

The measured data has to be read from data loggers, special bus systems or connections to specially purchased software packages (AgilentVee / LabView).
Data in summary reports of analytical investigations are discontinuously expected. Many analyzer-instruments and working methods of laboratory professionals prefer an evaluation in tabular form, the data from this area should therefore be exchanged in spreadsheet formats.
The field of plant control lets one expect data of both above procedures.

Especially by use of continuous measuring systems, it is neither sensible nor practicable to include all measured values as data in the data base. In specific cases data consolidation methods (not compression algorithms!) have to be applied to the measured values. For example, it may be useful, to insert a date into the data base only then, if the underlying measuring value has changed significantly. The significance depends on the responsiveness and resolution of the sensor and also on the required quality of data for simulation purposes.
The data have to be filtered based on mathematical methods. The goal is, to detect outliers in measuring series of whole data sets of faulty measuring devices and to eliminate them. Furthermore, the possibility to cross-analyze between different measurement-series has to be provided. The joint evaluation of several different sensor-data series simultaneously in a joint analysis should be enabled. Thereby, physical parameters derived from the real measuring values will also be inserted into the data base. Otherwise, it is to be examined whether it is possible to assess the quality of sensors by this joint-evaluation. It is expected that through correlation of several parameters, the need for recalibration of individual sensors will be detected by observing a slight deviant behaviour. Such a detection system would be a real gain in the implementation of measurements. The use of methods such as principal components analysis, discriminant analysis, regression procedures, (multi-sensor) data-fusion, latent semantic indexing, and so on is recommended.
The storage of data has to be accomplished in a way that maintains the topological, temporal and geometric properties. This is for future input data generation of crucial importance.

4.2 Providing data for the simulation

The proposed numerical simulations discretize the problem along the pipe geometry (spatially), as well as in time. A simulation requires initial conditions for each discrete point and boundary conditions as well as values for sink and source terms at discretized points in time. The input parameters have to be obtained from the values stored in the data base. The hurdle to be overcome is the adjustment of the measured values from the data base with the discretized model, because generally no coincidence of measurement points or measurement times to the discretization can be expected. In agreement with the hydrodynamic model implementation, a constraint generator is to be written, that produces the required values through interpolation and integration and serves them in the required form to the simulation.

4.3 Evaluation of model quality

The hydrodynamic simulation will be carried out for various periods and during this, the model parameters will be tuned, so that a good correlation to real behaviour of the wastewater system is obtained. The quality of the correlation will be rated by evaluating statistical methods comparing the data of data base against the results of the simulation. Statistical indicators for prediction quality are to be calculated, so that different simulation models can be compared in their performance. This is needed for calibration and validation of numerical models.

4.4 Data storage technology

The amount of expected data requires - regarding to scalability - a carefully chosen storage technology. It is important, to achieve an almost linear behaviour, so that no bottlenecks associated with growing data volumes arise.

The documentation of the trial run over several years is a value that has to be protected. It is proposed, to install the data management redundantly, so that the same systems are installed for the primary as well as for the reference pipe track. Given this, the data sets should be mutually replicated. Nevertheless, a data backup system should independent of it deployed.

4.5 Conclusions of data processing

The authors of this feasibility study strongly agree on the necessity to implement an integrated data processing and storage system. Large data sets, documenting sensorial and analytically won measurements, are emerging in the process of monitoring sewage systems for control of odour and corrosion. Units of data have to be reasonably and automatically captured and pre-processed. They form the basis for any calibration and validation of the numerical models, as well as the foundation to assess the model-quality. Since a comprehensive study investigating the field of data processing was not targeted, only a short depiction of the required tasks and the potential approaches are given.

Chapter 5

Countermeasures

If planners think odour and corrosion problems are likely to arise or if there are already problems, countermeasures have to be taken. Basically, planners can take the following into account:

- treatment of sewage
    - to prevent formation of H_2S,
    - to eliminate H_2S or
    - to inhibit its transfer to atmosphere
- treatment of gas or
- use of corrosion-resistant material.

Respective countermeasures are described below. This report focusses on measures that are in widespread use or have been established recently.

5.1 Sewage treatment

The aim of sewage treatment is to change odour-promoting conditions by shifting values of the parameters illustrated in sec. Chapter 2. Concepts of the measures that proved to be effective will be described below.

Table 9, Table 10 and Table 11 show a selection of technical possibilities to prevent odour and corrosion problems. For some of the measures, good practical experience has been made. Other ones have to be looked at in more detail. A complete controlled application with a measurement of the corrosion ratio or sulphate concentration has not been tested yet. It is important, that for each chosen measure the specific local conditions have to be adjusted to technical and economical aspects. The advantages and disadvantages of each system have to be considered. In addition to theoretical reflections, practical comparable tests can be very helpful. Just in the last few years, an increasing number of new measures are traded, so that a neutral consultation, trial and a critical assessment should be requested. Preventive or operational methods to minimise odour and corrosion emergence are often not considered during the planning phases neither under technical aspects nor under economical aspects, so that most of the costs incurred have to be paid out of the operational budget.

Table 9: Measures in the planning phase to reduce Odour and corrosion in sewers [BARJENBRUCH, 2002 expanded]

Measure	Operation mode	Remarks
Reduction of the emission sources	- reducing numbers of shafts - limitation of max detention periods	- location - could cause a different problem
Pressure drainage systems	- closed sewer system - reduction to max. one transferring ponit.	- selective and accurate treatment of exhaust water
Competent constructing of pumping stations	- maintaining state in case of aerobic waster water; avoid turbulence in case of anaerobic state	- often limited effects
Vacuum drainage systems	- Prevention of H_2S development by constant aerobic transport	- Limited length of the system - high precision in constructural laying of the pipes - problem of detecting leaks
Care of conventional roof ventilation	- specific ventilation of the channels by ventilating the house drain of each individual buildings	- generally, sanitary public health engineering standard; has often not been taken into consideration recently
Pneumatic pumping station	- applying compressed air in order to pump wastewater - always aerobic conditions	- higher investments

5.1.1 Enrichment and preservation of oxygen in sewage

The method of this measure is to keep sewage “fresh”. If there is a sewer atmosphere rich with oxygen, generation of turbulences dissolves oxygen in water. This can be achieved by installation of baffles, cascades or falls e.g. at inlets of collecting tanks of pumping stations (s.

Figure 23), if there is abundant slope. Special options for problematic rising-mains are blowing-in of pressurised air or technical oxygen, compressed air flushing or a vacuum drainage systems instead of direct water pumping.

Another procedure is to augment redox potential of wastewater by dosage of chemicals. There are various chemical compounds increasing redox potential of a solution. First dosage of technical oxygen was applied, but insufficiently spreading in the water phase is a considerable disadvantage. Dosage of non-volatile products are easier to handle. The definite market leading procedure in Germany is the dosage of a $Ca(NO_3)_2$–solution called Nutriox®. In addition to this, potassium permanganate, ozone, hydrogen peroxide, sodium chloride and sodim hypochlorite are stronger oxidants in use. Another approach is to admit building-up of H_2S and to eliminate it prior to the point of disturbance. The Thiox-method consists of the dosing of an oxidating substance (e.g. oxygen) at the last section of a pressure pipe. Sulphide oxidating bacteria dominate under these conditions and metabolise a relevant part of H_2S. Some bacteria species that are involved in removing of odourous sulphur compounds have been identified and proved to enhance odour reduction [GENG et al., 2004, FRIEDRICH et al., 2004]. All fresh keeping methods have in common that oxidation of organic compounds decreases the fraction of readily biodegradable compounds, which can be necessary at the treatment plant for biological phosphorous elimination and denitrification.

5.1.1.1 Nitrate demand

YANG & HOBSON (2001) propose a calculation for nitrate demand. Underlying the demand of dissolved oxygen cited from POMEROY (1990) (2 mg/l/h respictively 700 mg/ m²/h), they assume that oxygen-respiring microorganisms are capable to catabolise nitrate, too. For an equivalent number of electron receptors, 1 mg/l of nitrate-nitrogen can replace approximately 2.86 mg/l of dissolved oxygen. Therefore, the equivalent nitrate consumption rates for sewage and biofilm are 0.7 mg/l/h of NO_3^--N and 250 mg/m²/h of NO_3^--N respectively. With these values and estimations for nitrate respiration rates, nitrate demand by a forced main can be calculated:

$$M = \pi \frac{D^2}{4} LR_S + \pi DLR_B = 0.00025\pi DL(0.7+1)$$

M - - Total nitrate demand [kg NO_3^--N/h]

D - Inner diameter of the rising main [m]

L - Length of rising main [m]

R_S - Nitrate respiration rate of sewage [kg NO_3^--N/m³/h]

R_B - Nitrate respiration rate of biofilm [kg NO_3^--N/m²/h]

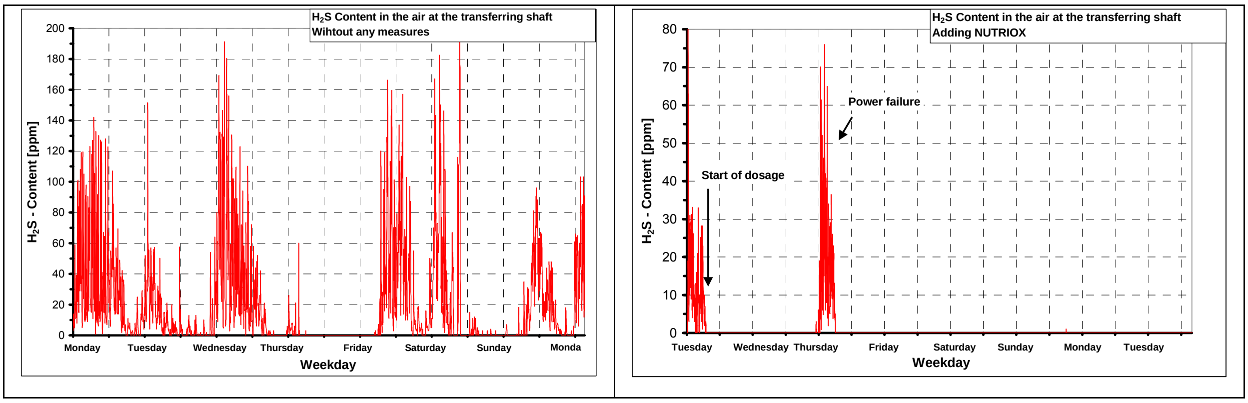


Figure 13: H_2S contents in the end of a pressure pipe
left: reference phase without dosage; right: dosage of NUTRIOX

5.1.1.2 Dosage of $Ca(NO_3)_2$ – Nutriox®

The dosage of $Ca(NO_3)_2$ will be explained in detail, because it is the most applied oxidation agent. Veolia Eau Germany employs 800 t/a and only one town in Northern Germany applies 42 t/a.

Respiration of dosed nitrate results in a higher yield of energy. Bacteria using this catabolism succeed against fastidious sulphate-reducing and fermenting bacteria. Thus no osmogens (from H_2S or organic acids) emerge, but molecular, volatile nitrogen. For this reason, gas cushions can evolve, if rising mains are not vented adequately. For operation of this measure, a place for a batcher is necessary where a reaction time of at least 40 minutes can be assured. In addition, the batcher needs access to water supply and a bus bar. This chemical is low hazardous to waters and lachrymatory. A double wall storage tank is therefore obligatory. This measure has proved high effectiveness and solves unspecific odour problems, too. Costs are relatively high [ATV, 2003]. YANG & HOBSON (2001) point out, that it is hard to satisfy nitrate demand in sewage systems with intermittent flow regimes, because nitrate is delivered and transported by sewage flow. When flow stops, so does the supply of nitrate. Meanwhile, life goes on in the rising main and exhausts nitrate.

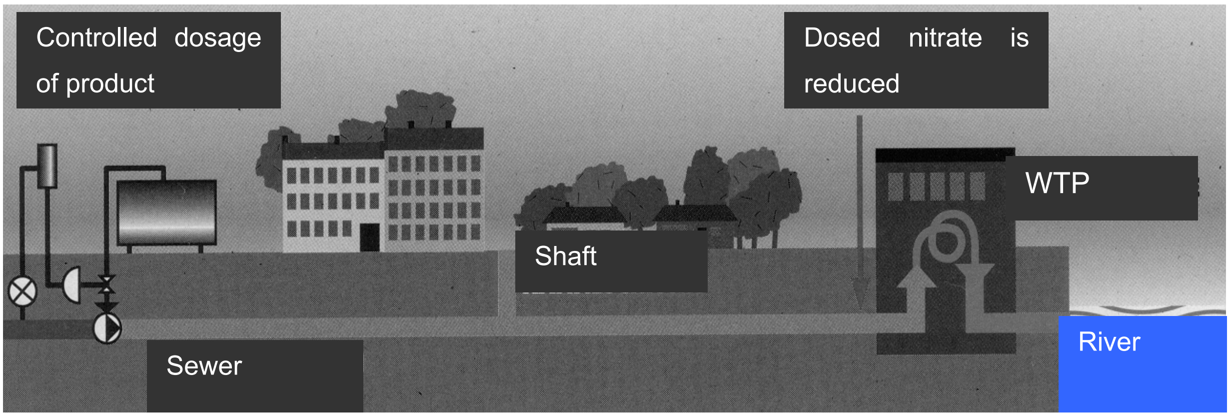


Figure 14: Principle of nitrate dosage

5.1.2 Precipitation

Iron salts (s. Table 10) are used as precipitants to bind the already generated sulphide as iron sulphide. It is an adequate coagulant, because its solubility is lower than other ferric compounds in water. The reaction depends on pH. Between pH 7 and 8, least dosage of iron is necessary. It is a selective reaction to reduce H_2S, therefore other odour-causing substances are not affected. Some combined products like solution of $Na[Al(OH)_4] + FeCl_3$, ferric nitrate (sold as Anaerite 263®) use both mechanisms: stabilisation of redox potential and flocculation (see below).

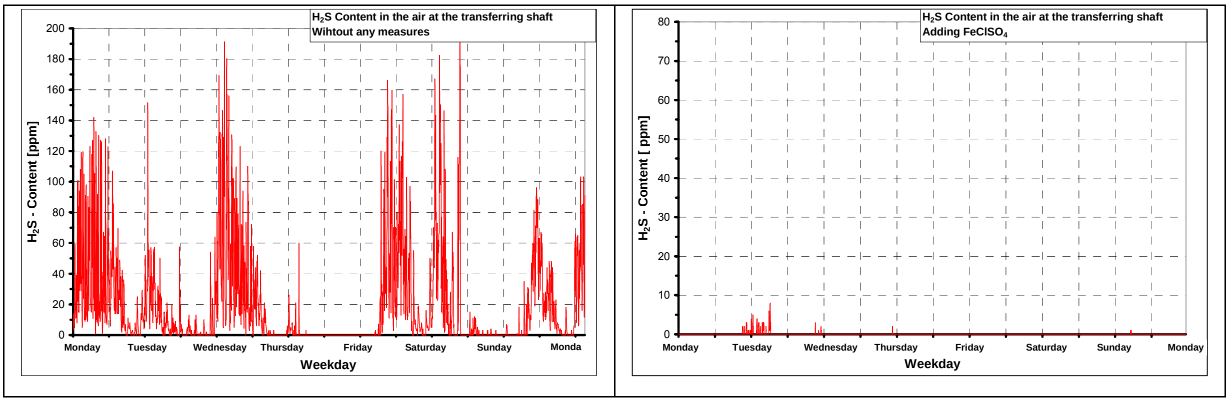


Figure 15: H$_2$S contents in the end of a pressure pipe
left: reference phase without dosage; right: FERRIFLOC dosage

Dosage of iron salts

Iron salts are applied in solid or in liqid form. Solutions of iron II sulphate, iron II chloride, or iron III chloride sulphate are employed. Agents only react with the already developed sulphide, that is still in water phase. Like for Nutriox-dosage, a batcher, a bus bar, water supply and handling of a chemical that is low hazardous to water, have to be provided. In addition, the acid solution requires corrosion resistant materials. Hindered settling causes expansion into wastewater treatment plant, where it can reduce demand for precipitation agents for phosphor elimination.

Stoichiometric equation for dosage of trivalent iron is:

$$2\,Fe^{3+} + 3\,H_2S \rightarrow 2\,FeS + 6\,H^{+} + S$$

It follows as above, a theoretical demand of 1.17 mg Fe^{2+} per mg S^{2-} [ATV, 2003]. Daily demand for precipitation agent is calculated with the following formula:

$$Q_{d(FM)} = \frac{c(S^{2-}) * M_{Fe} * Q_d}{M_S * \frac{V_{Fe}}{V_{FM}} * \zeta_{FM}}$$

$Q_{d(FM)}$ - daily demand for precipitation agent [l/m³ sewage]

$c(S^{2-})$ - concentration of the sum of sulphide, HS$^-$ and H$_2$S in sewage [mg/l]

Q_d - daily wastewater flow [m³/d]

M_X - molar mass of substance x [u]

$\frac{V_{Fe}}{V_{FM}}$ - volume portion of iron of precipitation agent [-]

ζ_{FM} - density of of precipitation agent [g/cm³]

Dosage of iron nitrate

Nitrate and ferric suppress development of H_2S through different mechanisms and acting in sequence. Therefore, an extra value may be achieved when they are supplied as the single agent $Fe(NO_3)_3$. As both ions of this salt hinder odour nuisance, demand for the combined chemical should be reduced compared to FeCl or $Ca(NO_3)_2$. It did not turn out like this in practice. One reason is that there is no constant ratio between H_2S-concentration and nitrate demand. YANG & HOBSON assume a possible delay of action by ferric following nitrate exhaustion Therefore, theoretical savings are not achievable. A moderate saving of 5 to 15 % may be possible [YANG & HOBSON, 2001]. Similar observations were made by MATSCHÉ (2004) who determined a three times higher demand in practice, than theoretically calculated. In addition, specific costs are between 400 and 790 €/t, i.e. higher than for Nutriox ®. Iron nitrate is available as “Anaerite” from VTA and ACAT.

5.1.3 pH-regulation

The augmentation of pH withdraws hydrogen from H_2S (s. sec. 2.1.2). The resulting ions HS^- and S^{2-} are not volatile. Dosage amounts based on the pK_a-values underestimate demand for pH-increasing chemicals. YANG & HOBSON (2001) hypothesise that pH at the water surface (point of H_2S-transfer) is directed by CO_2-transfer. This way, the alkaline boundary water layer prevents stripping of H_2S, while an acid pH is measured in the bulk of the water. pH-regulators in use are mentioned in Table 10.

5.1.4 Reduction of biofilms

Submerged biofilms have the major part in oxygen consumption [YANG & HOBSON, 2001], shortening the time span until fermentation starts. That is why there are countermeasures restricting deposition or removing deposits. There are field trials to inhibit sedimentation in rising-mains with quickly varying electromagnetic fields. To build the inductor, sewers are wrapped with a conductor. Installation is possible in full operation [ECS; ROSENWINKEL, 2007]. Some mechanical means are listed in Table 10. VOIGT (2007) reports a measure especially for separate systems: installations to allow a directed discharge of the stormwater at beginning of sewer or at points with sedimentation.

Table 10: Sewage treatment to reduce odour and corrosion in sewers [Barjenbruch, 2002 expanded]

Measure	Operation mode	Remarks
Oxidants	technical oxygen (only to be used in closed pressure pipes) Thiox-method; dosing of an oxidant at the last section of the pressure pipe Nutriox® in form of $Ca(NO_3)_2$	preventing anaerobic processes consumption of organic carbon compounds reliable method relatively high costs gas bubbles can block the pipe
	Ozone (toxic, AGW value 0,1 ppm) hydrogen peroxide (H_2O_2) (limited stability and explosion hazard) potassium permanganate ($KMnO_4$) NaCl+NaOCl; production of AOX, effective for a short period only sodium hypochlorite (NaOCl, germicidal, possible production of AOX	oxidation of the reduced sulphur compounds increased consumption due to reaction with other wastewater compounds; high costs of purchase slight sustainability
Precipitation agents	ferric chloride sulphate solution, ferric sulphate solution, ferrous chloride solution $Fe(OH)_3$ as sludge or conditioned sludge (dosing of solid substances requires individual test)	dissolvable iron sulphide is produced; it works specific on H_2S additional sludge at wastewater treatment plant reducing pH-value and acid capacity sustainable method; effective also in downstream network
Regulators of pH-value	increase of the pH-value by using lime milk, hydrated lime production of sulphide is prevented from appr. pH< 9,5 (short reaction time) caustic soda solution, sodium aluminate	stripping of ammonia is possible precipitation is possible pH online measuring is advised only effective as long as pH-value is at high level in downstream network section the pH will increase again (expensive dosage point)
Combined products	Kemwater-Anaerite (product based on Fe and NO_3^-) Sachtleben company (Al+ NO_3^-) ABS-product ($Na[Al(OH)_4]$ + $FeCl_3$ VTA-Dolomin (solution of NO_3^- $+Ca^{2+}$ + Mg^{2+})	have hardly been tested; combine advantages and disadvantages of the respective basic materials
Products to compensate odour	products to mask odour; covering unpleasant odour compensation or fixation	effect is disputed and depends on individual attitude no effect which protects from corrosion
Biological active agents e.g. enzymes	microorganisms, enzymes, plant extracts, tensides (used as a biocatalyst); inhibitors	mostly not effective little experience

Belonging to table 10:

Measure	Operation mode	Remarks
Cleaning of the channels	removal of depositions and biofilm in the channel with shields, ploughs, high pressure rinsing surge flushing with automatic flap gate or others cleaning of pressure mains with big balls or small balls of expended clay	limited effect constant repetition necessary requires a lot of personnel and equipment addition of inhibitors
Installing a (rotating) contactor	reducing substances with high odour load which can be easily degraded	requires more maintenance clogging and blocking
Adding external water (drinking water, pump water or surface water)	reducing detention time reducing concentrations in wastewater for a short period and increasing oxygen concentration	requires more energy increases the quantity of wastewater not according to the law adapting to precipitation is necessary

5.2 Gas treatment

Sewer networks are vast plants and odourous gases spread easily in this atmosphere. For this reason:

- countermeasures have to be installed in a large area or
- problematic gases should be focused at certain points, where gas is treated.

Figure 16: Gel plates before installation in Hanover [ROSENWINKEL, 2007]

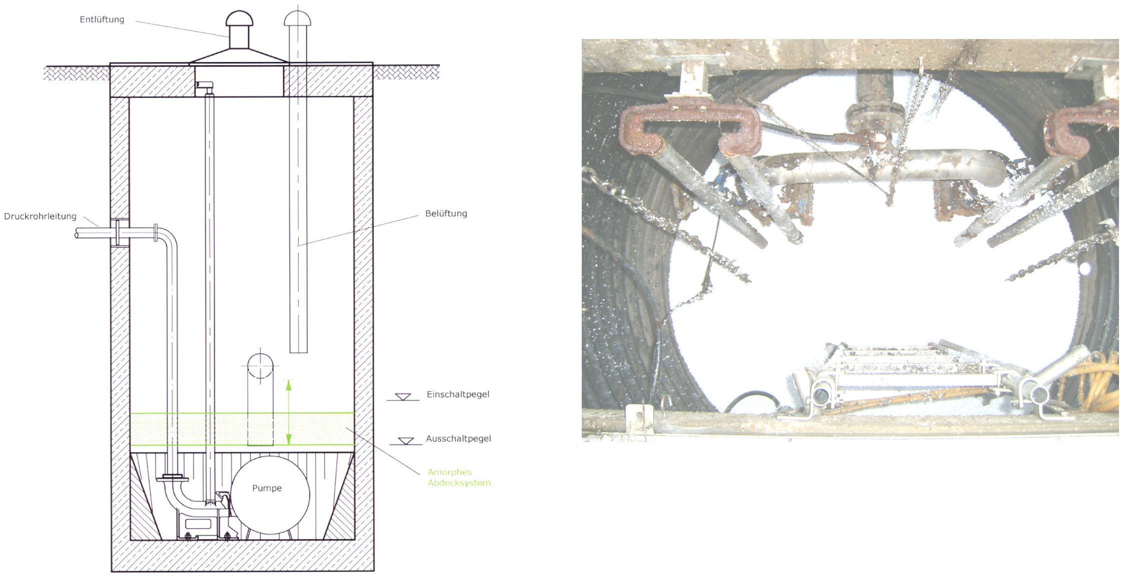


Figure 17: Principle sketch of amorphous covering system

Examples for extensive measures are installations of coverings or gel plates. **Gel plates** (BIOTHYS) contain essential oils (terpene alcohols, aldehydes and ketones). Odourous substances react to them and form compounds, which smell less intense [BIOTHYS]. To ensure the reaction, gel plates need sufficient air ventilation. Therefore, ROSENWINKEL (2007) recommends to hang gel plates in shafts right in front of a pump. Gel plates have to be replaced every 2 to 4 months [BIOTHYS]. For the DRAUSY-measure a perforated tube is pulled into a gravity sewer. Afterwards air or another oxidant is distributed to keep aerob conditions [LAWA, 2004].

There are **covering systems** available that are installed inside the manhole. They seal the manhole with a plastic to avoid escape of gases. A rest of air circulation is manually adjustable. The type of covering systems that are installed close to the base of the manhole have the advantage to beware the shaft from corrosion. A third type is an amorphous covering system. It consists of a swimming layer of particles that constrict gas transfer. They are used in pumping stations.

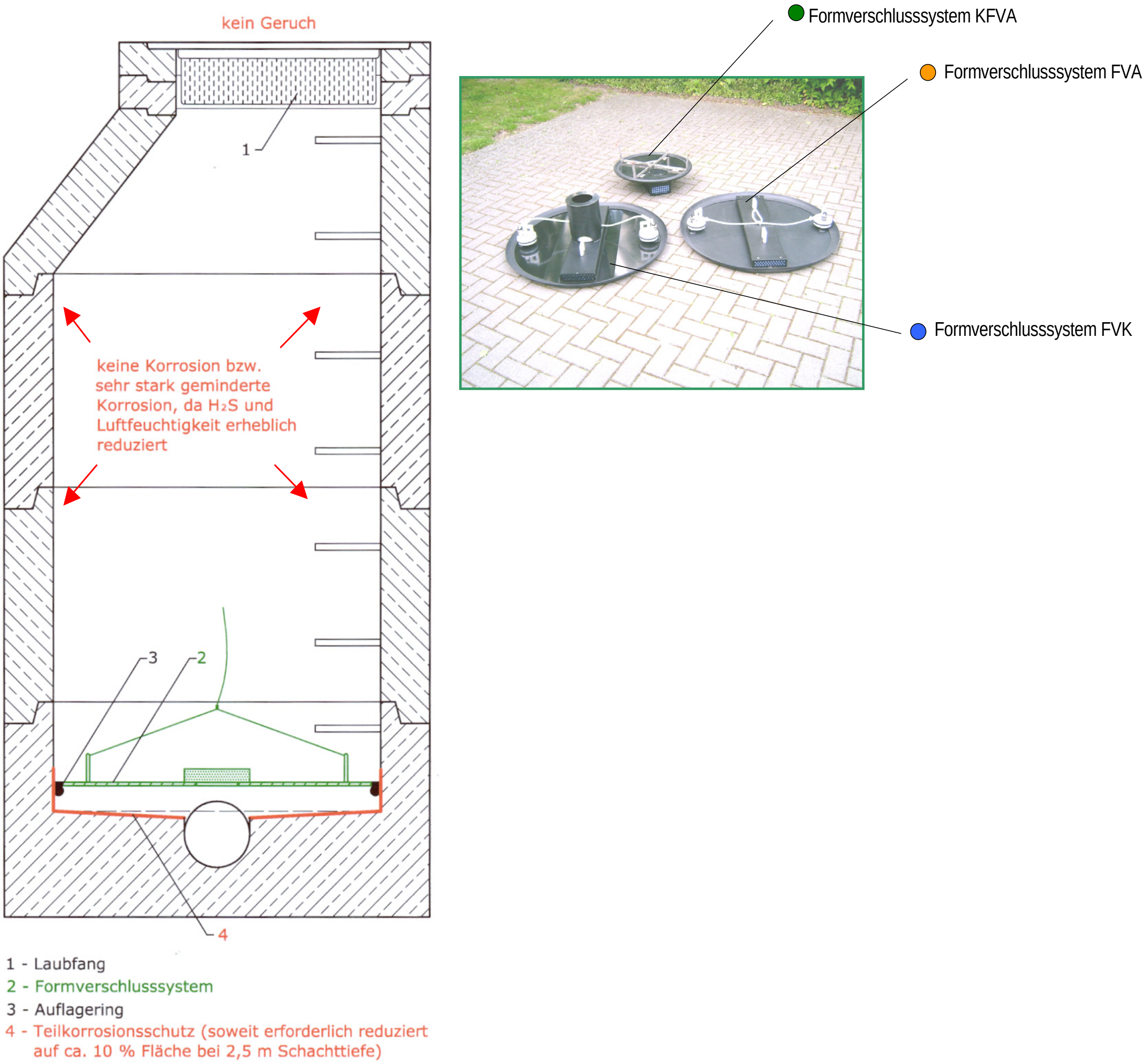


Figure 18: Principle sketch of shaft closing system and photo of various types

Before searching for an adequate method of gas *treatment*, one should note, that risk for complaints can be reduced, choosing well directed points for exhausting air. For this purpose manholes with **enlarged ventilation openings** should be installed in areas where odour can not become a nuisance for the population. Flowing wastewater is able to carry along the airstream above in the sewer. If sewer atmosphere has access to fresh air, it can provide a certain amount of oxygen. This natural ventilation can be promoted by installation of manholes with enlarged ventilation openings at adequate points [VOIGT, 2007]. This is one example for constructive enrichment of the O_2-concentration.

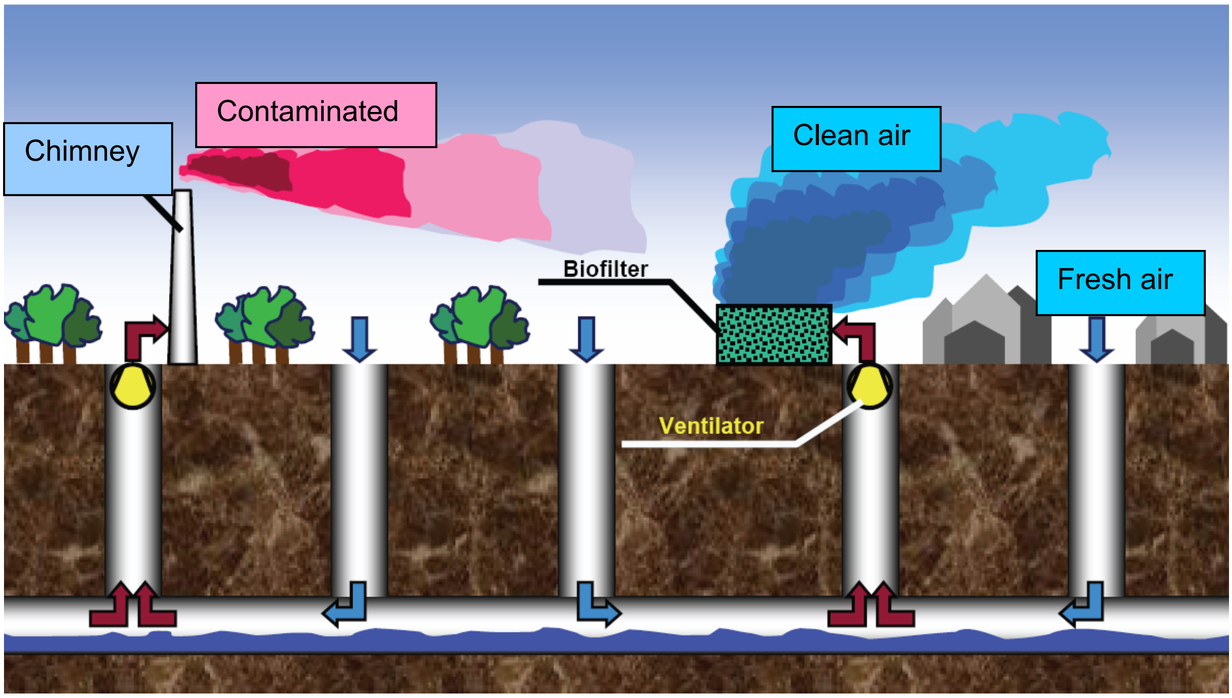
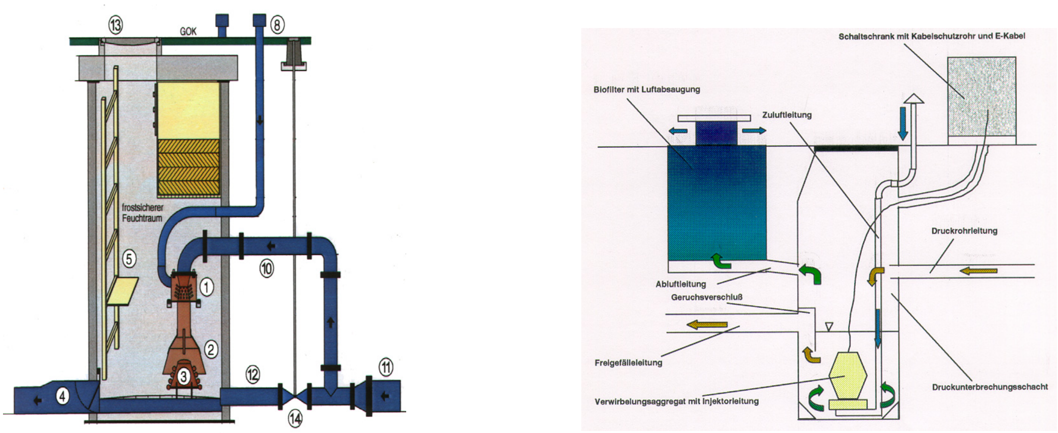


Figure 19: Forced ventilaton by chimney and ventilator [FRANK, 2007]

If the location of escaping odours is reduced to few spots, a specific gas treatment can be applied. This is possible at vent openings of rising mains, at pump stations or at points where flow changes. There is a variety of scrubbers (STUETZ & FRECHEN, 2001). Their strategy is to oxidise or to sorb sulphur-compounds.

There are biofilters in use with and without forced air stream. Odourants are bound to materials such as bark mulch, peat, expanded clay etc. Carrier material has to be kept wet.

Another adsorbent is activated carbon. Its surface can be modified by impregnation, catalytic substances, gas-injection or with immobilised sulphide-oxidating bacteria [YAN et al., 2004; STUETZ & FRECHEN, 2001]. In Sydney´s pumping station a catalytic incineration of odourous gases utilising a platinum catalyst is in operation. One measure uses **photooxidation**. Constituents of exhaust air are cracked by radiation with ultraviolet light. In this process emerging strong oxidants like oxygen- and hydroxyl-radicals result in destruction of odourous substances. Photooxidation functions also in combination with ozone treatment. Furthermore, there are biotrickling filters, biofilters and bioscrubbers in use as they are known at wastewater treatment plants. Special bioscrubbers blow odourous gases even through bioreactors of activated sludge [STUETZ & FRECHEN, 2001].



without electrical energy

with electrical energy

Figure 20: **Stripping of H_2S at a selected manhole**

Table 11: **Measures in gas phases to reduce odour and corrosion in sewers [Barjenbruch; 2002 expanded]**

Measure	Operation mode	Remarks
Specific stripping with exhaust air treatment	stripping at points with change of flow (drop, vacuum aeration) selective treatment of waste air (biological or chemical scrubber)	reduced hydraulic efficiency is possible space at the surface is needed; additional operation point, energy requirement possible
Covering systems	stripping of H_2S is prevented is applied in pump stations and manholes	odour nuisance is limited to the place where the covering systems are applied
Treatment inside manhole	exhaust air is treated with on-the-spot-biofilters or gel plates in the manhole	corrosion of network cannot be reduced; maintenance is necessary, odour will be transferred to other emersion points
Compressed air flushing	difference of head-loss about 4-6 bar (BÜHLER system) reduction of the detention time in pressure pipe removal of the biofilm	has to be taken into consideration when planning the pressure pipe increased investments for compressed air stations
Installing a (rotating) contactor	reducing substances with high odour load which can be easily degraded	requires more maintenance clogging and blocking
Care of conventional roof ventilation	specific ventilation of the channels by ventilating the house drain of each individual buildings	generally, sanitary public health engineering standard, that has often not been taken into consideration recently

5.3 Choice of building material

The right choice of building material helps to reduce the threat of corrosive attack. BELIE et al. (2004) have shown that pipes out of concrete with limestone aggregates buffer against acidification. Therefore, their application has advantages compared to inert materials[VOIGT, 2007]. Materials like thermoplastic (PE, PVC, PP), polymerconcrete, fibreglass reinforced plastic, and coatings out of thermoplastics, elastomeres or glas should be prefered. Another aim is to reduce moisture of the upper sewerwall to hinder sulphid-oxidating bacteria. BELIE et al. (2004) proved that concretes with low values of water absorption are favourable too. Detailed information on specific materials is given below.

5.3.1 High-resistant concrete, corrosion protection systems

One way to minimise damage caused by biogenic acid corrosion, is the use of high-resistant concrete. It is often assumed, that concretes with high compressive strength would automatically be concretes with high resistance against chemical attack. Correct is only that concretes with high-density and durability are usually high strength concretes, but not necessarily vice versa.

With use of high-performance concrete as a "monolithic corrosion protection system" two criteria must be met to ensure high long-term stability of reinforced concrete components against chemically-corrosive attacks:

- The high-performance concrete must have a maximum chemical resistance of the binder-agent matrix to the possible attacks of inorganic and organic, chemically corrosive substances. Quartz aggregates are nearly inert against acid chemical attacks compared to the binding-agent matrix. For this reason the resistance of concrete is mainly determined by the binding-agent matrix.
- The high-performance concrete must have maximum water tightness to act against the penetration of possibly corrosive chemical substances. This is achieved through a dense packaging of the total concrete structure right into the finest particles. At the same time, a minimization of vulnerable binding-agent is achieved

On behalf of RWE Energie AG a highly durable concrete with maximum possible acid resistance was developed at Technische Universität Berlin, in cooperation with MPA Berlin Brandenburg.

With highly durable concrete built of optimally chosen materials and w/z-values between 0.38 and 0.42 a resistance can be achieved, that is approximately 5-to 20 times higher compared to "traditional" concretes based on CEM I HS. The lifespan increases directly in proportion to the resistance, too. Above all, no sub-surface-damage to the binding-agent matrix takes place when highly durable concrete is applied. The sub-surface damage of the highly resistant concrete corresponds to the depth of the visible damage.

Figure 21 shows two examples of concrete slabs after about 6 months of exposure to sulphuric acid pH 2. The concrete on the left in Figure 7 shows a concrete with approximately 380 kg HS CEM I, w / z-value 0.42. The concrete on the right in Figure 7 is a concrete with optimized resistance, densest packing of the overall mix, low binding-agent content and binding-agent with maximum resistance, compared to acid. Whereas “conventional" concrete shows degradation, the optimized concrete shows a virtually intact surface with only a salt-crust deposit.

Conventional concrete
380 kg cement, w/z=0,42

Optimized concrete
320kg BM: Z+FA+MS, w/b=0,42

Figure 21: View of concrete slabs after 6 months of exposure to water with sulphuric acid content (approx. pH = 2). Left: strong degradation. Right: practically intact surface only with salt-crust deposit.

In 1999, in Niederaussem near Cologne, there was the highest cooling tower in the world (200 m) built without further corrosion protection on the inside. See also: HILLEMEIER, B., HÜTTL, R.: High performance concrete - An example of acid resistance. Concrete Plant + Precast Technology, 66 (2000), H. 1, S. 52-60.

Sewage plants and prefabricated parts for sewage plants with the usual required life span can be built with optimized resistant concrete if the pH-value caused by biogenic acid production does not slip under approx. 3.5 to 4. With strong biogenic sulphuric acid corrosion pH-values can partly reach up to 0.5. Compared with a pH-value of 3.5, this is thousand fold of acid-ion- concentration. Compared to the natural pH-Value of concrete (about 12.6 at CEM I, and about 12.4 at CEM III B), this is an approximately ten trillion fold! acid-concentration (H^+ concentration).Under such conditions, concrete must be supplemented with a corrosion protection system, against a further attack of sulphuric acid.

Chapter 6

Feedback control systems

Regulation and adjustment of countermeasures are generally based on information from suppliers, who provide partly commercial material. Therefore, this type of information is doubtful. The particular setting for each application is determined by experience and trial and error [YANG & HOBSON, 2001]. Complaints about odour nuisance are documented and evaluated. Subsequently, H_2S-concentration of the sewer atmosphere is measured to estimate the demand on countermeasures. Afterwards an apparently suitable countermeasure is implented. Control measurements are carried out to adjust the countermeasure. A more objective and transferable decision process that is applicable for most cases and types countermeasures should be prefered. It is introduced below.

If it is foreseeable during the planning phase or if problems with odour and corrosion occur within a certain sewer network, the operator has to decide:

1) Does the intensity of odour and/or corrosion make a technical countermeasure or rehabilitation necessary?
2) Which measure is adequate?
3) To what extent, this measure has to be carried out?

The risk of odour and corrosion depends on parameters that can be regulated by a feedback control system. This kind of control system is supplied with

- data about the kind and state of the material of the network and
- data about the influencing conditions.

These data are combined with information about the relations between parameters, results and costs of treatments, resulting in commands to trigger the measure. Afterwards, data about impacts of the measure is collected and analysed. This way, feedback information enables improvement of the control system.

Criteria for odour assessment

To assess number 1) it has to be mentioned, that there are no generally valid and accepted criteria to distinguish between relevant and irrelevant odour nuisance. The province Nordrhein-Westfalen in Germany has passed a regulation for residential areas for assessment of odour nuisance. It demands to determine the frequency and time spans of odours. Accordingly, odours emerging with a frequencies of less than 3 % of the hours of a year have to be tolerated [MUNLV, 2004]. (Odours causing health impact because of feeling sickness are an exception.) After emergence from the liquid phase, H_2S

spreads and gets transformed, depending on weather, gas pressure and ventilation. Not till then, the odour infiltrates and is smelled. Principally, concentration of H_2S decreases during transmission. Therefore, it proved to be practical to aim at a concentration of less than 3 ppm in sewer atmosphere to assure to go below the threshold-odour concentration of 0.13 ppm H_2S in respirated air [BARJENBRUCH, 2006].

Adjustment of countermeasure

To answer number 3) one has to keep in mind, that especially for measures with dosage of chemicals, adjusting the right amount of dosing is the critical factor. Excessive dosage has to be avoided because it is wasteful and unwanted side-effects are not justifiable anymore [STUETZ & FRECHEN, 2001]. The task to find the right amount for dosing is not trivial, as generation and sorption of H_2S at sewer wall does not occur steadily and there is e.g. no fixed ratio between concentration of sulphide-species and nitrate needed [YANG & HOBSON, 2001]. Furthermore it was observed that short peaks of very high H_2S-concentrations cause odour problems, meanwhile more than 90% of the time H_2S-concentrations are close to zero. HVITVED-JACOBSEN (2002) assumes that the reason is the fast degradation of H_2S in the biofilm. Adjustment to these very short periods of odour nuisance is difficult.

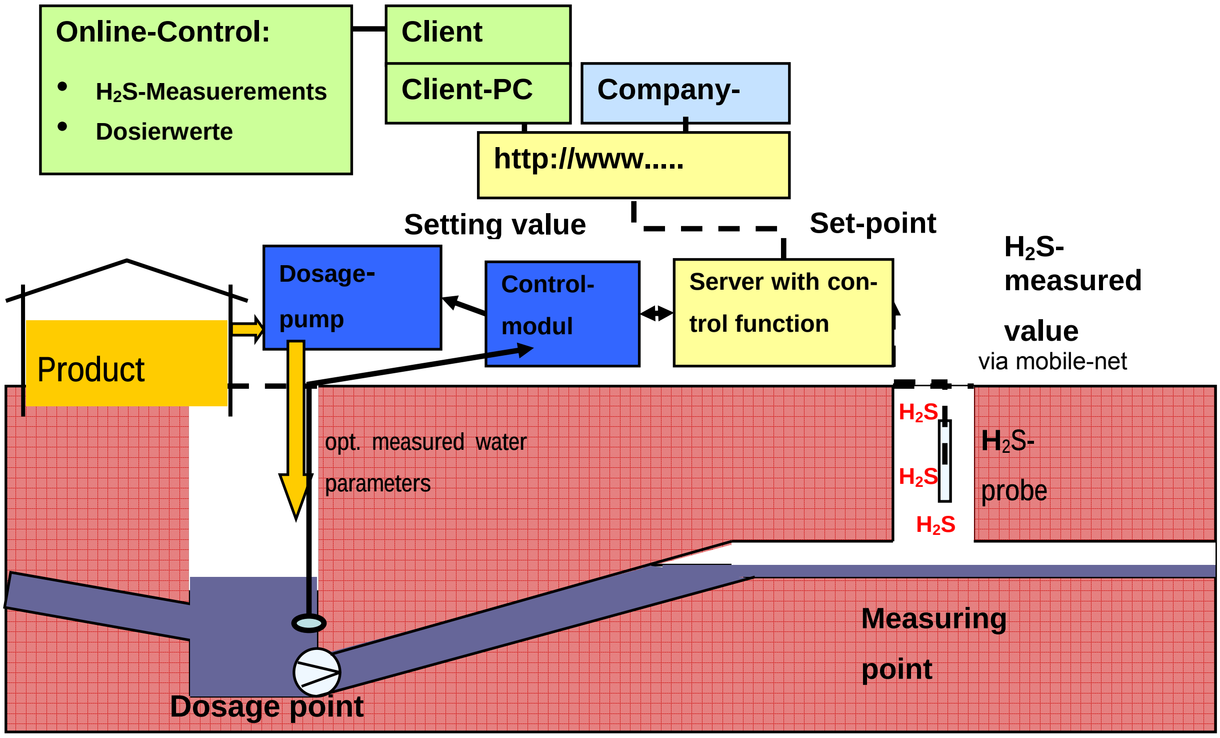


Figure 22: **On-Line Control of the dosage of chemical products**

Source: VTA-Hartmann

Examples

A conventional approach would be to start with a survey of the status quo. IATROU et al., (1997) in Houston/Texas took samples of sewage and shaft atmosphere, analysing sulphide and H_2S for decision-taking. In Martinez (USA) SMITH et al. (2004) combined examination methods of physical investigation, H_2S-measure in sewer headspace and sulphide measure in sewage. With help of a model [ASCE, 1989], they calculated expected lifetime of several sections of the sewer network. Some sections demanded immediate rehabilitation by installation of PVC sheet liner, slipliner pipe and others. Other sections showed to have more than 0,635 cm of “sacrificial concrete”. Operators opposed the estimated costs for measures to reduce H_2S-concentration to certain levels to savings by extended lifetime. The District chose the 0.3 mg/l dissolved sulphide control level. Dosage of hydrogen peroxide and caustic slugging were applicated and adjusted by continous measurement of H_2S in sewer atmosphere.

The producers of precipitation agents VTA, KRONOS and Südflock utilise the parameters H_2S-concentration and temperature of sewer atmosphere and temperature of sewage after point of dosage, to plan and to adapt required quantity.

There are also some trials to adjust countermeasures online without time gap. FRECHEN (2007) tests at Emschergenossenschaft a control system, using the parameters odour emission potential and H_2S-concentration of sewage and H_2S-concentration in gas phase after point of dosage. For determination of odour emission potential odours are stripped out of the liquid phase and measured with sensor arrays of an electronic nose (see sec. 3.2.2.4).

Yara sells a control system that consists of “long-nose” a control unit and dosage of $Ca(NO_3)_2$. They include parameters of H_2S-concentration in sewer-atmosphere and detention time [MATSCHÉ, 2007]. Variation of certain parameters with time is considerable. Efforts have been taken to integrate certain weekly patterns of parameters in control systems [MATSCHÉ, 2007; STUETZ & FRECHEN, 2001]. They focus on temperature, sewage flow and composition, as there is knowledge about their time variation. It is imaginable to add diurnal or yearly patterns.

An example that has find its way into official rules is described below. Generation of turbulences by falls can be controlled by a level-depending switching mechanism for the pump. Furthermore, if there is data about state of aerobicity of the wastewater (e.g. the information, that a slaughterhouse is discharging wastewater with a high content of BOD at the moment), fill-levels can be adjusted (s.

Figure 23).

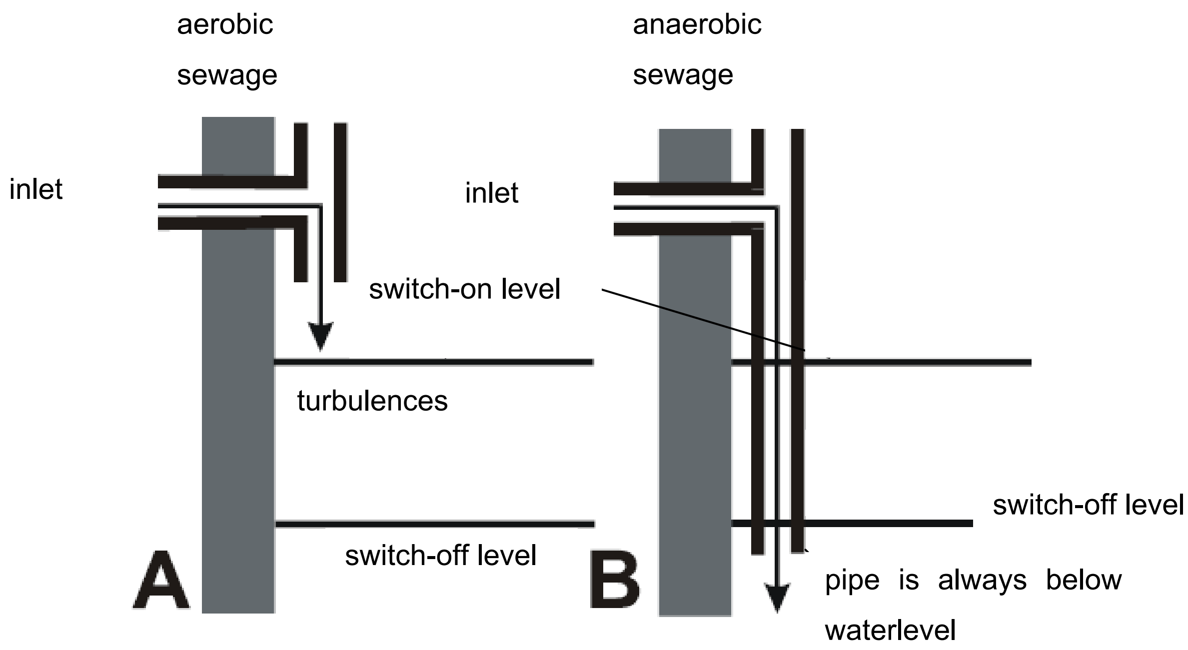


Figure 23: Controlled inlets in pumping stations [THISTLETHWAYTE, 1979]

Other parameters that could be considered

Beside fill level, adjustment of flux could be oriented towards quality of wastewater to ensure that e.g. the time span during very readily biodegradable constituents are stored is shortened [VOIGT, 2007]. If dosing of a chemical is the chosen counter-measure, the aim of regulation could be to keep a minimal concentration of the agent downstream of the critical area [YANG & HOBSON, 2001].

It can be concluded, that deeper knowledge about relationships between parameters and odour or corrosion, including knowledge about kinetics of these processes, would be helpful to adjust countermeasures automatically for savings of wasteful amounts. A reliable prediction technique based on modelling, could support this.

Chapter 7

Modelling

First, we start with an overview on empirical formulas which are applied to estimate the sulphide development in sewers. There is a number of models which have a ‘certain’ relation to flow, transport and reaction processes in sewers and the associated odour and corrosion problems. These models stem from the fields of urban drainage, wastewater plants and water-quality models. We give an overview on these models also commenting on the different requirements for modelling odour and corrosion in sewer systems. Then, we focus on the very few models which have a ‘closer’ relation to odour and corrosion in sewer systems, we introduce one model which is already comparatively far developed in this direction and we also point out the model’s limitations.

All models which are mentioned in the following are written in capital letters and are listed in the appendix.

7.1 Estimation approaches for sulphide development

In order to estimate the development of odour and corrosion to be expected in sewage systems, several empirical approaches to sulphide development have been suggested [BARJENBRUCH & DOHSE, 2004].

In **gravity sewers**, the sulphide development depends primarily on the pipe circumference submerged in biofilm, and with a limit of 15% maximum, no sulphide problems arise in practice. Significant parameters for the computational estimation procedure, for example after POMEROY (1970), for the determination of the corrosion parameter Z_P are the biochemical oxygen demand BOD_5 (mg O_2/l), the wastewater temperature T (°C), the partially filled wastewater flow quantity Q_T (l/s), the bed slope I_S and a function value f, consisting of the width of the water level b (m), the submerged pipe circumference u_{hydr} (m) and the quotient of the partially filled wastewater flow quantity and the flow quantity when completely filled. The evaluation of the result of the rule of thumb given by POMEROY (1970) with regard to the corrosion that is to be expected is summarized in Figure 24.

$$z_P = \frac{\left(BOD_5\right) \cdot 1{,}038^{\,(1{,}8 \cdot T - 36)}}{\sqrt[3]{35{,}31 \cdot Q_T} \cdot \sqrt{I_S} \cdot f\left(\frac{t}{D}\right)} \qquad f\left(\frac{t}{D}\right) = 1{,}4 \cdot \frac{b}{u_{hy}} \cdot \left(\frac{Q_T}{Q_V}\right)^{0{,}064}$$

Z_P = parameter of corrosion according to Pomeroy
I_S = bed slope of the drain
b = width of the wastewater surface [m]
u_{hy} = submerged pipe circumference [m]
Q_T = flow when partially filled [m³/s]
Q_V = flow when completely filled [m³/s]

< 5 000	very low sulphide content	no corrosion
~ 7 500	sulphide content of several 1/10 mg/l possible in areas with strong turbulence	slight corrosion
~ 10 000	in areas with strong turbulence	medium corrosion
~ 15 000	in areas with strong turbulence	severe corrosion
≥ 25 000	in areas with strong turbulence	very severe corrosion

Figure 24: POMEROY'S rule of thumb for the determination of the corrosion parameter Z_P in gravity sewers, after THYSTLETHWAYTE (1972)

For the purpose of practical estimations in pressure mains, various calculation procedures have been suggested internationally and nationally, some of which provided considerably diverging results. The divergence was caused mainly by the input parameters. Thus the ATV-DVWK 116's approach includes only flow time and diameter, whereas other authors include BOD_5, sulphate content, temperature, flow time, diameter and velocity of flow. The respective approaches are described below.

ATV (1992)

$$\Delta S = C \cdot t/D \qquad [mg/l]$$

C = 2,0 for pressure pipes
C = 1,0 for pipes flushed with pressed air
t = flow time [min]
D = diameter of pipe [cm]

US EPA (1991)

$$S_2 = S_1 + M \cdot (t_2 - t_1) \cdot [BOD_5 \cdot 1{,}07^{(T-20)} \cdot (4/D + 1{,}57)] \qquad [mg/l]$$

S_2 = concentration of sulphide at time t_2 [mg/l]
M = empirical coefficient for surface flow of sulphide [m/h]
$t_2 - t_1$ = flow time [h]
4/D = 1/hydraulic radius of pipe [1/m]
T = temperature [°C]

POMEROY

$$d[S]/dt = 1{,}0 \cdot 10^{-3} \cdot [BOD_5] \cdot (1{,}07)^{(T-20)} \cdot 4/D \cdot (1 + 0{,}3\ D) \qquad [mg/(l \cdot h)]$$

$$C_S = BOD_5 \cdot 1{,}07^{(T-20)} \cdot (1 + 0{,}39\ D) \cdot t / (F \cdot D) \qquad [mg/l]$$

F = 250 at flow times between 1h and 5h
F = 666 at flow times between 0 and 10 min

BOON and LISTER

$d[S]/dt = 0{,}228 \cdot 10^{-3} \cdot [COD] \cdot (1{,}07)^{(T-20)} \cdot 4/D \cdot (1 + 0{,}37\ D)$ [mg/(l·h)]

$C_S = (COD \cdot 1{,}07^{(T-20)} \cdot (1 + 0{,}37\ D) + t) / (f \cdot D)$ [mg/l]

f = 1,096 at flow times between 1h and 5h
f = 2,900 at flow times between 0 und 10 min

THISTLETHWAYTE

$d[S]/dt = 0{,}5 \cdot 10^{-3} \cdot v\ [BOD_5]^{0{,}8}\ [SO_4]^{0{,}4} \cdot (1{,}14)^{(T-20)} \cdot 4/D$ [mg/(l·h)]

$C_S = v\ [BOD_5]^{0{,}8}\ [SO_4]^{0{,}4} \cdot (1{,}139)^{(T-20)} \cdot t / (500 \cdot D)$ [mg/l]

S = concentration of sulphide in gaseous phase [mg/l]
C_S = sulphide concentration in wastewater flow [mg/l]
SO_4 = concentration of sulphide [mg/l]
T = temperature [°C]
t = flow time [h]
D = diameter of pipe [m]
4/D = 1/hydraulic radius of pipe [m]
v = velocity of flow [m/s]

HADJIANGHELOU et al.

$\Delta S = 0{,}975 \cdot t/D$ [mg/l]

$\Delta S = 0{,}67 \cdot t^{1{,}07} \cdot 1{,}07^{(T-20)} / D$ [mg/l]

The authors state that the values are at least half and at most double the calculated value, and that therefore a safety factor of 2 is necessary [HADJIANGHELOU et al., 1984].

NIELSEN, HVITVED-JACOBSEN and RAUNKJAER

$r_S = 4{,}0 \cdot 10^{-3} \cdot (COD - 47)^{0{,}49} \cdot \theta^{(T-20)}$ [g S/(m²·h)]

r_S = production of sulphide [g S/(m² ·h)]
COD = chemical oxygen demand [g O_2/m³]
T = temperature [°C]
θ = 1,07 = correction factor for temperature (Nielson, Hvitved-Jacobsen (1988)).

Following further measuring in pressure mains, Nielsen et al. (1998) develop another formula for the estimation of sulphide production:

$r_S = a \cdot (COD - 47)^{0{,}5} \cdot \theta^{(T-20)}$ [g S/(m²·h)]

θ = 1,03 = correction factor for temperature
a = parameter depending on quality of sewage

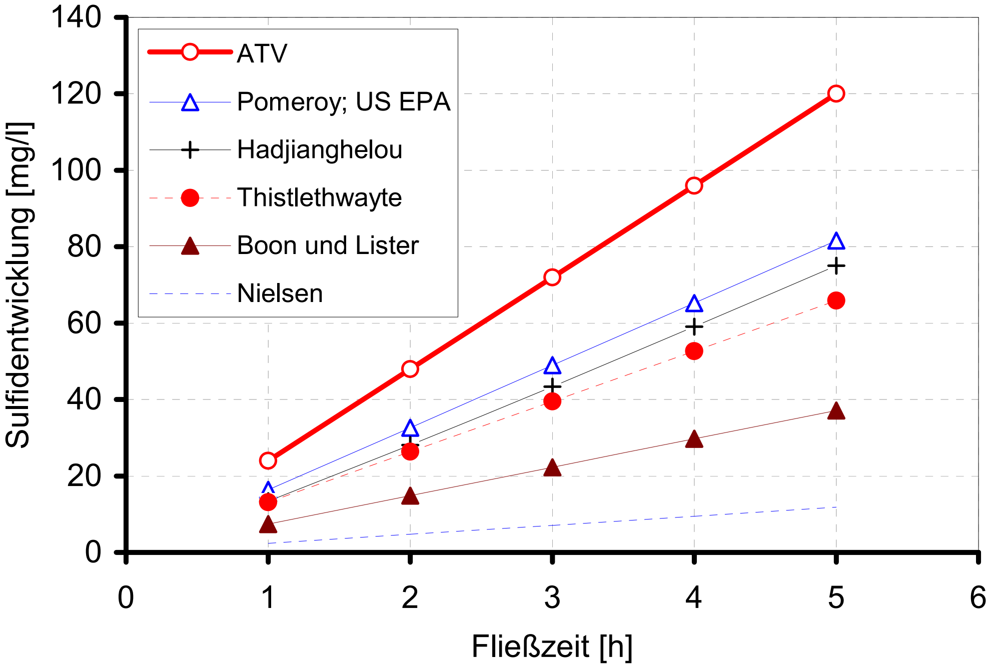


Figure 25: Comparison between different approaches for the determination of theoretic sulphide development depending on the flow time in a pressure main [DOHSE, 1999]. Sulfidentwicklung means build-up of sulphide, Fließzeit means flow time.

All approaches calculate the total amount of sulphide, which does not necessarily have to be stripped out into the canal atmosphere. A comparison in Figure 25 shows that, under equal boundary conditions (t_R = 5 h), the approach according to ATV produces values which are approx. 50% higher, so that the approach used has to be carefully tested. In the following Figure 26, a comparison of measured and calculated hydrogen sulphide concentrations is shown for different approaches. For analysing this figure, one has to take into account that the axes for the measured and calculated hydrogen sulphide concentrations are different. Regression lines have been determined for the measurements and calculations. The very low correlation coefficients for all approaches indicate their very poor agreement [LAWA, 2004].

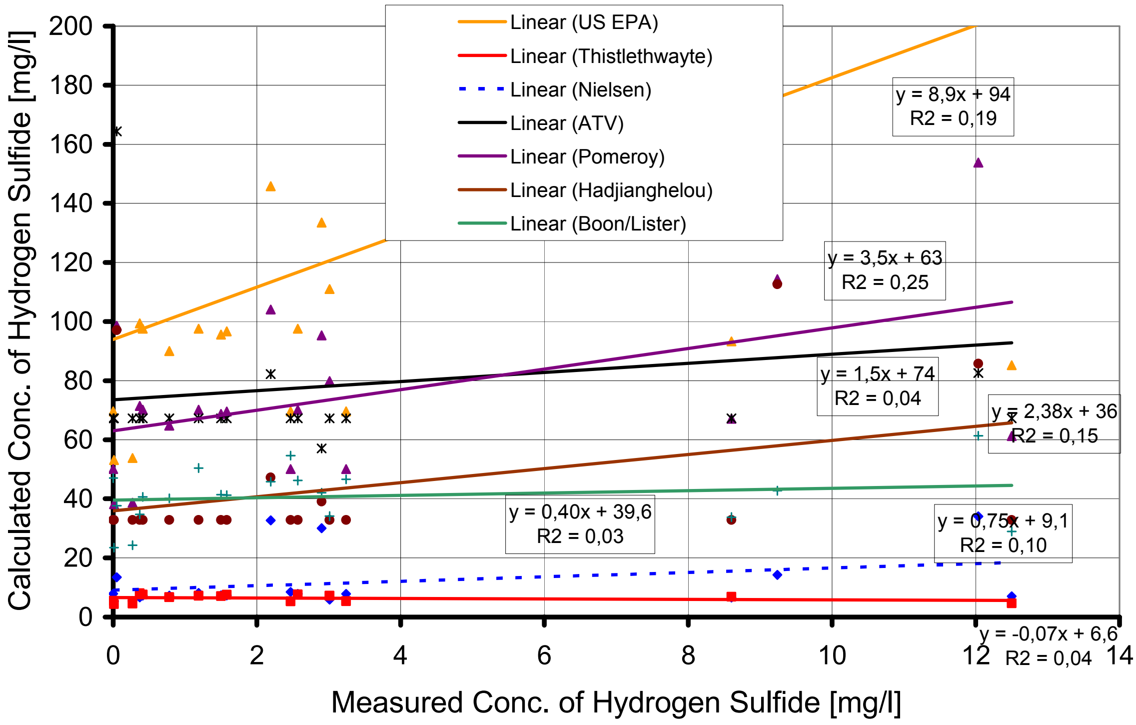


Figure 26: **Comparison of measured and calculated concentrations of hydrogen sulphid for different approaches (attention: different scaling in horizontal and vertical direction)**

There is a number of empirical formulas for the prediction of hydrogen sulphide in both, gravity sewers and pressure mains. However, the formulas are rather limited to very specific conditions and they are hardly transferable to general conditions. Therefore, they are a means to get a very rough estimation, but they are not suitable for a more precise prediction of odour and corrosion in sewer systems.

7.2 Urban-drainage models

Urban drainage models are already widely used in engineering practice and science of water resources management. They are applied in urban areas and they are similar to rainfall-runoff models which are used in river basins or in rural areas. In general, the processes and model concepts are very similar for urban drainage and rainfall-runoff models. Well-known rainfall-runoff models are MIKE SHE [REFSGAARD et al., 1995], WASIM-ETH [SCHULLA et al., 2006] or NASIM [WOLF-SCHUMANN, 1994]. An overview on urban-drainage models is given in ATV DVWK M 165 (2004), SCHÜTZE (1998) and RAUCH et al. (2001), well-known urban-drainage models are MOUSE / MIKE-URBAN, HYSTEM-EXTRAN, INFOWORKS-CS or STORM [INGENIEURGESELLSCHAFT SIEKER, 2003]. Urban-drainage and rainfall-runoff models simulate runoff generation and concentration in a catchment. Several models are also capable of simulating polluting loads. Thus runoff (and polluting loads) is (are) transported to sewer systems (in urban-drainage models) and to rivers (in rainfall-runoff models). In the following, we concentrate on the urban-drainage models.

In the sewers, we distinguish hydrological and hydraulic model concepts for simulating the flow and polluting loads. Hydrological models are based on translation or retention concepts, for example linear storage or storage cascasdes. They are computationally 'cheap' and therefore, they are a very good means, for example for long-term simulations. As the hydrological model concepts only give integral information on the scale of a catchment, a sub-catchment or a comparatively coarse grid (e.g. 1x1km), they are not suitable for our purposes because we require refined information about flow fields and concentration distributions.

Hydraulic models in sewers are based on the solution of the one-dimensional (stationary or instationary) continuity and momentum equations including concepts for turbulence. If we have gravity sewers, i.e. a free-surface in the sewer, the above-mentioned equations can be simplified to the so-called Saint-Venant or shallow-water equations, see for example the models EXTRAN, HEC-RAS. Sometimes, the Saint-Venant or shallow-water equations are not fully solved in sewer systems, but in a simplified form. It is mentioned that the flow in rivers is also based on the shallow-water equations. However, the equations are solved for rivers in one, two or three dimensions depending on the problems. This means that a hydraulic one-dimensional river model is suitable for modelling pipe flow without any modifications as soon as we have gravity sewers. For pressure mains, we do not solve the Saint-Venant, but the (one-dimensional) continuity and momentum equations, also called (one-dimensional) Navier-Stokes or Reynolds equations, for an incompressible fluid, see the models SIR 3S or EPANET [ROSSMAN, 2000], freely available from the US EPA (Environmental Protection Agency). If a sewer system consists of gravity sewers and pressure mains, the corresponding model concepts must be combined, see the models (SWMM 5, freely available from the US EPA), SIMBA-Sewer (see also sec. 7.5), STORM. For the practical use of a hydraulic model, the consideration of special buildings like weirs, culverts, pumping stations etc. is very important.

The simulation of gas flow in pipes is similar to the simulation of water flow in pressure mains. However, gas is considered instead of water and generally, the compressibility must be taken into account. Models come from the field of gas-supply (SIR 3S) or from the field of ventilation of shaft in coal mines [INWET, POLLACK, 1987]. To the nowledge of the authors, there is no model which simulates 'independent' water and gas flow in a pipe or gravity sewer.

In the literature, hydraulic models are also called hydrodynamic-numerical or HN or hydro-numerical models, while the models which solve the Navier-Stokes or Reynolds equations (in two or three dimensions) are also called CFD (Computational Fluid Dynamics) models.

Hydraulic models are based on the numerical solution of the underlying partial differential equations, generally based on the Finite-Difference (FDM), Finite-Element (FEM) or Finite-Volume method (FVM) or combinations of these methods. Therefore, a mesh is generated for the computational domain which subdivides the domain into cells (FDM) or elements (FEM) or control volumes (FVM) where the unknowns, for example the flow velocities or the concentrations, are computed on the corresponding nodes. In recent years, the FVM has become more and more popular in hydro- and environmental engineering because it guarantees local conservation behaviour, while the FEM is ‘only’ globally conservative. Both methods, FVM and FEM, are applicable to unstructured grids which should be chosen if the computational domain has complex boundaries or complex inner structures. The FDM as the only solution method is losing on importance as it is not necessarily conservative and restricted to structured grids. An overview on simulation methods for modelling hydro- and environmental systems is given in HINKELMANN (2005). If we compare hydraulic and hydrological models, the hydraulic ones require (much) more computational effort. However, they compute detailed information about the water level distribution and the flow fields depending on the chosen mesh resolution.

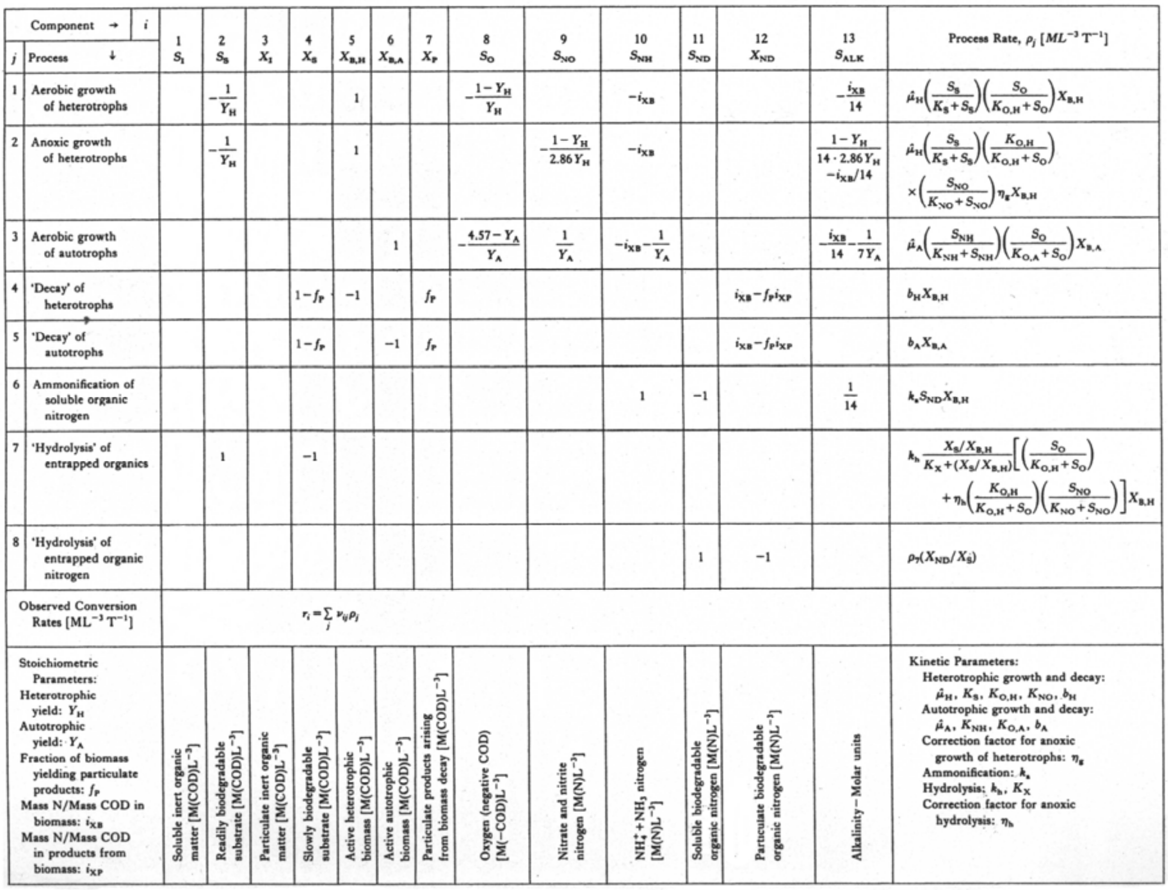
The polluting loads in the catchment are simulated with accumulation and removal approaches and thus they reach the sewer systems. Polluting loads in sewers can be modelled in a similar way as the flow with hydrological and hydro-numerical methods. For the same reasons as already mentioned in the context of the flow simulations, the hydrological concepts are not suitable for our purposes. The hydro-numerical concepts for transport consist of the numerical solution of the transport equation with the methods already mentioned (FDM, FEM, FVM and combinations). Principal transport mechanisms are advection, diffusion / dispersion and reaction. The transported components include dissolved and particulate ones. Particulate components can be deposed and eroded. Reaction processes could be based on concepts similar to the ones from the ASM family (see next section). As the reaction processes are poorly understood today, as they require many data and as they seem to be not relevant for several purposes which are not concerned with odour and corrosion, they are neglected in many models and just conservative transport is simulated.

The STORM model has a special emphasis on polluting loads based on different hydrological concepts. It also includes the relevant special buildings like storage-space channels, passage or storage basins. The SIMBA Sewer model forsees hydrological and hydro-numerical components for polluting loads including sedimentation and erosion. However, reaction processes in sewer systems have not been considered in both models (STORM, SIMBA Sewer; personal communications with the developers). Reaction processes in sewer systems are only accounted for in very few models. This will be discussed together with the aspect of data in sec. 7.6.

For our purposes of modelling odour and corrosion, we require a *hydro-numerical* model which is capable to simulate a detailed resolution of the flow processes (distribution of water levels and flow velocities) and the transport processes (concentration distributions of pollutants or other components). The *Finite-Volume method* is desirable because of its local conservation behaviour. As we just plan one-dimensional modelling, and computers have become fast in the last years, we generally do not expect to get problems with CPU times for most of our investigations.

7.3 Wastewater-plant models

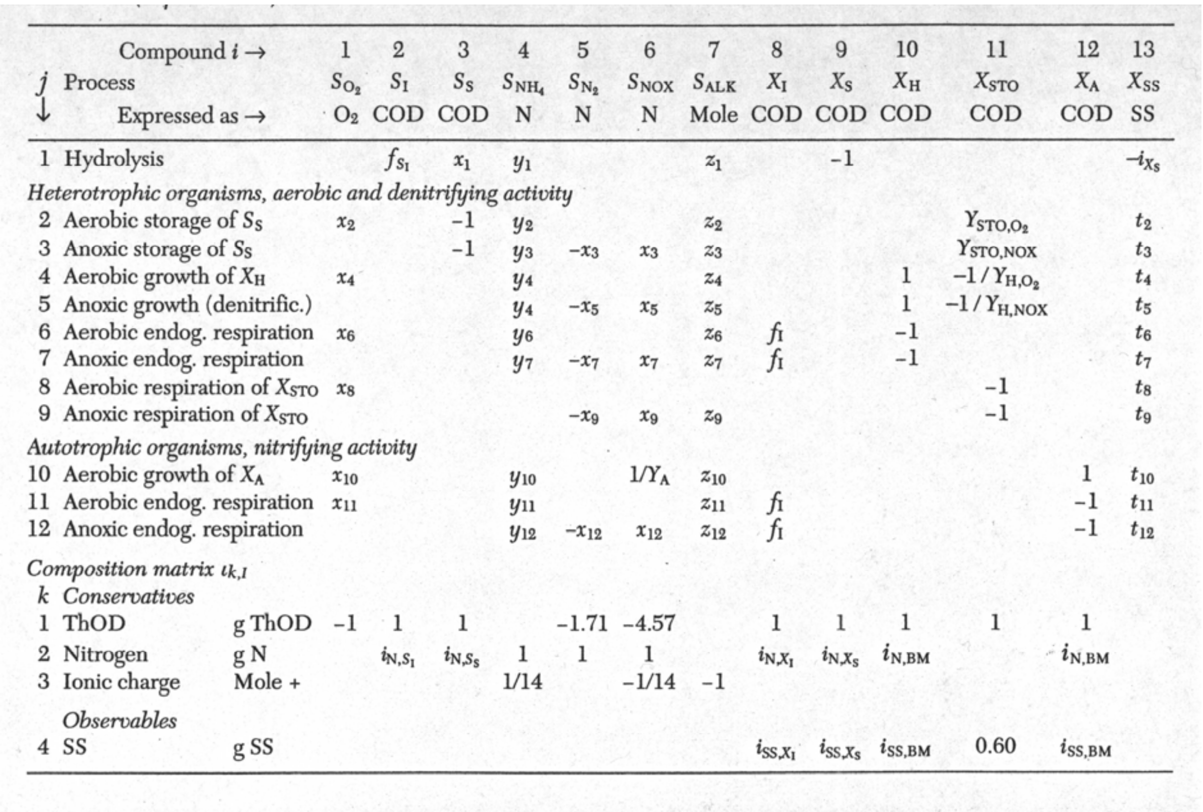
The hydraulics in wastewater plants is often simulated as a single or a series of fully mixed stirrer vessels. Sometimes one-dimensional hydro-numerical concepts as already introduces before are chosen. In the transport-reaction modelling, diffusion / dispersion is often neglected. The biochemical transformations are based on the ASM concepts (activated sludge model). ASM1 which has been developed by Henze et al. (1987) covers the carbon and nitrogen cycle. It solves the transport-reaction or mass-balance equations for 13 components based on the description of 8 processes (see Figure 27).



j	Component → i Process ↓	1 S_I	2 S_S	3 X_I	4 X_S	5 $X_{B,H}$	6 $X_{B,A}$	7 X_P	8 S_O	9 S_{NO}	10 S_{NH}	11 S_{ND}	12 X_{ND}	13 S_{ALK}	Process Rate, ρ_j $[ML^{-3}T^{-1}]$
1	Aerobic growth of heterotrophs		$-\frac{1}{Y_H}$			1			$-\frac{1-Y_H}{Y_H}$		$-i_{XB}$			$-\frac{i_{XB}}{14}$	$\hat{\mu}_H\left(\frac{S_S}{K_S+S_S}\right)\left(\frac{S_O}{K_{O,H}+S_O}\right)X_{B,H}$
2	Anoxic growth of heterotrophs		$-\frac{1}{Y_H}$			1				$-\frac{1-Y_H}{2.86Y_H}$	$-i_{XB}$			$\frac{1-Y_H}{14\cdot 2.86Y_H}$ $-i_{XB}/14$	$\hat{\mu}_H\left(\frac{S_S}{K_S+S_S}\right)\left(\frac{K_{O,H}}{K_{O,H}+S_O}\right)$ $\times\left(\frac{S_{NO}}{K_{NO}+S_{NO}}\right)\eta_g X_{B,H}$
3	Aerobic growth of autotrophs						1		$-\frac{4.57-Y_A}{Y_A}$	$\frac{1}{Y_A}$	$-i_{XB}-\frac{1}{Y_A}$			$-\frac{i_{XB}}{14}-\frac{1}{7Y_A}$	$\hat{\mu}_A\left(\frac{S_{NH}}{K_{NH}+S_{NH}}\right)\left(\frac{S_O}{K_{O,A}+S_O}\right)X_{B,A}$
4	'Decay' of heterotrophs				$1-f_P$	-1		f_P					$i_{XB}-f_P i_{XP}$		$b_H X_{B,H}$
5	'Decay' of autotrophs				$1-f_P$		-1	f_P					$i_{XB}-f_P i_{XP}$		$b_A X_{B,A}$
6	Ammonification of soluble organic nitrogen										1	-1		$\frac{1}{14}$	$k_a S_{ND} X_{B,H}$
7	'Hydrolysis' of entrapped organics		1		-1										$k_h \frac{X_S/X_{B,H}}{K_X+(X_S/X_{B,H})}\left[\left(\frac{S_O}{K_{O,H}+S_O}\right)\right.$ $\left.+\eta_h\left(\frac{K_{O,H}}{K_{O,H}+S_O}\right)\left(\frac{S_{NO}}{K_{NO}+S_{NO}}\right)\right]X_{B,H}$
8	'Hydrolysis' of entrapped organic nitrogen											1	-1		$\rho_7(X_{ND}/X_S)$
Observed Conversion Rates $[ML^{-3}T^{-1}]$		$r_i=\sum_j \nu_{ij}\rho_j$													
Stoichiometric Parameters: Heterotrophic yield: Y_H Autotrophic yield: Y_A Fraction of biomass yielding particulate products: f_P Mass N/Mass COD in biomass: i_{XB} Mass N/Mass COD in products from biomass: i_{XP}		Soluble inert organic matter $[M(COD)L^{-3}]$	Readily biodegradable substrate $[M(COD)L^{-3}]$	Particulate inert organic matter $[M(COD)L^{-3}]$	Slowly biodegradable substrate $[M(COD)L^{-3}]$	Active heterotrophic biomass $[M(COD)L^{-3}]$	Active autotrophic biomass $[M(COD)L^{-3}]$	Particulate products arising from biomass decay $[M(COD)L^{-3}]$	Oxygen (negative COD) $[M(-COD)L^{-3}]$	Nitrate and nitrite nitrogen $[M(N)L^{-3}]$	$NH_4^+ + NH_3$ nitrogen $[M(N)L^{-3}]$	Soluble biodegradable organic nitrogen $[M(N)L^{-3}]$	Particulate biodegradable organic nitrogen $[M(N)L^{-3}]$	Alkalinity – Molar units	Kinetic Parameters: Heterotrophic growth and decay: $\hat{\mu}_H$, K_S, $K_{O,H}$, K_{NO}, b_H Autotrophic growth and decay: $\hat{\mu}_A$, K_{NH}, $K_{O,A}$, b_A Correction factor for anoxic growth of heterotrophs: η_g Ammonification: k_a Hydrolysis: k_h, K_X Correction factor for anoxic hydrolysis: η_h

Figure 27: Process matrix for ASM1 [HENZE et al., 1987]

For the description of the reaction and processes, a matrix notation has been introduced and it has established for such kind of problems since then (see Figure 28).



	Compound $i \to$		1	2	3	4	5	6	7	8	9	10	11	12	13
j	Process		S_{O_2}	S_I	S_S	S_{NH_4}	S_{N_2}	S_{NOX}	S_{ALK}	X_I	X_S	X_H	X_{STO}	X_A	X_{SS}
↓	Expressed as →		O_2	COD	COD	N	N	N	Mole	COD	COD	COD	COD	COD	SS
1	Hydrolysis			f_{S_I}	x_1	y_1			z_1		−1				$-i_{X_S}$
Heterotrophic organisms, aerobic and denitrifying activity															
2	Aerobic storage of S_S		x_2		−1	y_2			z_2				Y_{STO,O_2}		t_2
3	Anoxic storage of S_S				−1	y_3	$-x_3$	x_3	z_3				$Y_{STO,NOX}$		t_3
4	Aerobic growth of X_H		x_4			y_4			z_4			1	$-1/Y_{H,O_2}$		t_4
5	Anoxic growth (denitrific.)					y_4	$-x_5$	x_5	z_5			1	$-1/Y_{H,NOX}$		t_5
6	Aerobic endog. respiration		x_6			y_6			z_6	f_I		−1			t_6
7	Anoxic endog. respiration					y_7	$-x_7$	x_7	z_7	f_I		−1			t_7
8	Aerobic respiration of X_{STO}		x_8										−1		t_8
9	Anoxic respiration of X_{STO}						$-x_9$	x_9	z_9				−1		t_9
Autotrophic organisms, nitrifying activity															
10	Aerobic growth of X_A		x_{10}			y_{10}		$1/Y_A$	z_{10}					1	t_{10}
11	Aerobic endog. respiration		x_{11}			y_{11}			z_{11}	f_I				−1	t_{11}
12	Anoxic endog. respiration					y_{12}	$-x_{12}$	x_{12}	z_{12}	f_I				−1	t_{12}
Composition matrix $\iota_{k,I}$															
k	*Conservatives*														
1	ThOD	g ThOD	−1	1	1		−1.71	−4.57		1	1	1	1	1	
2	Nitrogen	g N		i_{N,S_I}	i_{N,S_S}	1	1	1		i_{N,X_I}	i_{N,X_S}	$i_{N,BM}$		$i_{N,BM}$	
3	Ionic charge	Mole +				1/14		−1/14	−1						
	Observables														
4	SS	g SS								i_{SS,X_I}	i_{SS,X_S}	$i_{SS,BM}$	0.60	$i_{SS,BM}$	

Figure 28: Process matrix for ASM3 (IWA Task Group 2000)

A further step in that direction was ASM2 (HENZE et al. 1995) and ASM2d [HENZE et al. 1999] which included the biological and chemical elimination of phosphorus. As phosphorus will not be of importance for our purposes, we do not comment on it further.

ASM3 is not an extension of ASM2(d), but an extension of ASM1. It was developed by an IWA Task Group (2000) and it is an improvement of ASM1. ASM3 was also initiated by the IWA Task Group to serve as a platform for further developments. ASM3 includes the following processes: hydrolysis, aerobic and anoxic storage of readily biodegradable substrate, aerobic and anoxic growth of heterotrophs, aerobic and anoxic endogenous respiration, aerobic and anoxic respiration of storage products. The corresponding kinetic expressions are based on switching functions (hyperbolic or saturation terms, Monod equations, S/(S+K)). The switching functions stop all biological activity as educts of a processes approach zero concentrations, one important difference between ASM1 and ASM3. Models for percolating filters, primary clarifiers and clarifiers in wastewater plants are discussed in SCHÜTZE (1998) or RAUCH et al. (2001). One very important aspect for all models mentioned in this section is the fact that they all need many data which partially can be taken from the literature and partially must be measured for driving, calibrating and validating the models.

The SIMBA model is tool for the simulation of wastewater treatment plants which is widely-spread in research and engineering practice, especially in Germany. It includes ASM1, ASM2(d) and ASM3 as well as different other ASM variants. It foresees also several modules for the sludge treatment. It is further commented on in section 7.6. The two models DENIKAplus and DENISIM are a linked package for dimensioning, optimizing and simulation wastewater treatment plants. DENIKAplus mainly deals with aeration tanks and clarifiers, while DENISIM enables dynamic simulation concerning water purification based on ASM1 and ASM2d.

In many respects, a wastewater plant and a sewer are very similar concerning the occurring microbial processes. Therefore, the modelling concepts such as ASM can be similar, too. However, there are a number of aspects which are different concerning the definition of the system, dominating processes and a number of details. The heterotrophic biomass concentration in bulk water of a sewer is typically low compared to activated sludge. Substrate in a sewer may be relatively abundant. Easily biodegradable substrate is in 'young wastewater' often available for non-limited biomass growth.

7.4 Water-quality models

Water-quality models for rivers or lakes are also based on simulating flow and transport, and then they include different kinds of reactions. Most models are just one-dimensional, however, a few are also two- and three-dimensional. SCHNEIDER (1999) developed a one-dimensional model which simulates the effects of combined sewer overflow in rivers focussing on oxygen and ammonium. The one-dimensional model QSIM concentrates on the biological processes related to oxygen, nutrients, algae and zoo plankton including the interactions with the river bed [KIRCHESCH et al., 1999]. The one-dimensional WBALMO simulates more than twenty species or species groups and it has its focus on water quality problems related to post mining areas [KÖNGETER et al., 2004]. QUAL2K is a one-dimensional river and stream quality model with a wide range of reaction processes (freely available from the US EPA). The River Quality Model No. 1 (RWQM1) has been developed by an IWA Task Group [REICHERT et al., 2001] to formulate a standardized and consistent water quality models. It includes the important transformation processes of organic carbon, nitrogen and phosphorous compounds as well as physical processes such as sedimentation, resuspension, reaeration, gas exchange at weirs, overall 24 componentes and 30 processes, see Figure 29.

The multi-dimensional model CAEDYM is especially suitable for water quality in freshwater and marine ecosystems including many reaction processes [HIPSEY et al., 2006]. KOPMANN (1999) developed a water quality model for rivers also based on a three-dimensional flow model. She included several reaction processes of the ATV water quality model (ATV-DVWK 2002) and she dealt with the down-scaling of multi-dimensional water quality models. HUNZE (1996) developed a water quality model for an aeration basin on the basis of ASM1 [HENZE et al., 1987] and she coupled it with a multi-dimensional flow model.

No.	Process	Rate
(1a)	Aerobic Growth of Heterotrophs with NH_4	$k_{gro,H,aer,To} e^{\beta_H (T-T_0)} \frac{S_S}{K_{S,H,aer}+S_S} \frac{S_{O2}}{K_{O2,H,aer}+S_{O2}} \left[\frac{S_{NH4}+S_{NH3}}{K_{N,H,aer}+S_{NH4}+S_{NH3}}\right]\left[\frac{S_{HPO4}+S_{H2PO4}}{K_{HPO4,H,aer}+S_{HPO4}+S_{H2PO4}}\right] X_H$
(1b)	Aer. Gro. of Hetero. with NO_3	$\left[k_{gro,H,aer,To} e^{\beta_H (T-T_0)} \frac{S_S}{K_{S,H,aer}+S_S} \frac{S_{O2}}{K_{O2,H,aer}+S_{O2}} \frac{K_{N,H,aer}}{K_{N,H,aer}+S_{NH4}+S_{NH3}} \frac{S_{NO3}}{K_{N,H,aer}+S_{NO3}} \left[\frac{S_{HPO4}+S_{H2PO4}}{K_{HPO4,H,aer}+S_{HPO4}+S_{H2PO4}}\right] X_H\right]$
(2)	Aerobic Respiration of Heterotrophs	$k_{resp,H,aer,To} e^{\beta_H (T-T_0)} \frac{S_{O2}}{K_{O2,H,aer}+S_{O2}} X_H$
(3a)	Anoxic Growth of Heterotrophs with NO_3	$k_{gro,H,anox,To} e^{\beta_H (T-T_0)} \frac{S_S}{K_{S,H,anox}+S_S} \frac{K_{O2,H,aer}}{K_{O2,H,aer}+S_{O2}} \frac{S_{NO3}}{K_{NO3,H,anox}+S_{NO3}} \left[\frac{S_{HPO4}+S_{H2PO4}}{K_{HPO4,H,anox}+S_{HPO4}+S_{H2PO4}}\right] X_H$
(3b)	Anoxic Growth of Heterotrophs with NO_2	$k_{gro,H,anox,To} e^{\beta_H (T-T_0)} \frac{S_S}{K_{S,H,anox}+S_S} \frac{K_{O2,H,aer}}{K_{O2,H,aer}+S_{O2}} \frac{S_{NO2}}{K_{NO2,H,anox}+S_{NO2}} \left[\frac{S_{HPO4}+S_{H2PO4}}{K_{HPO4,H,anox}+S_{HPO4}+S_{H2PO4}}\right] X_H$
(4)	Anoxic Respiration of Heterotrophs	$k_{resp,H,anox,To} e^{\beta_H (T-T_0)} \frac{K_{O2,H,aer}}{K_{O2,H,aer}+S_{O2}} \frac{S_{NO3}}{K_{NO3,H,anox}+S_{NO3}} X_H$
(5)	Growth of 1st-stage Nitrifiers	$k_{gro,N1,To} e^{\beta_{N1} (T-T_0)} \frac{S_{O2}}{K_{O2,N1}+S_{O2}} \frac{S_{NH4}+S_{NH3}}{K_{NH4,N1}+S_{NH4}+S_{NH3}} \frac{S_{HPO4}+S_{H2PO4}}{K_{HPO4,N1}+S_{HPO4}+S_{H2PO4}} X_{N1}$
(6)	Aerobic Respiration of 1st stage Nitrifiers	$k_{resp,N1,To} e^{\beta_{N1} (T-T_0)} \frac{S_{O2}}{K_{O2,N1}+S_{O2}} X_{N1}$
(7)	Growth of 2nd stage nitrifiers	$k_{gro,N2,To} e^{\beta_{N2} (T-T_0)} \frac{S_{O2}}{K_{O2,N2}+S_{O2}} \frac{S_{NO2}}{K_{NO2,N2}+S_{NO2}} \frac{S_{HPO4}+S_{H2PO4}}{K_{HPO4,N2}+S_{HPO4}+S_{H2PO4}} X_{N2}$
(8)	Aerobic Respiration of 2nd stage Nitrifiers	$k_{resp,N2,To} e^{\beta_{N2} (T-T_0)} \frac{S_{O2}}{K_{O2,N2}+S_{O2}} X_{N2}$
(9a)	Growth of Algae with NH_4	$k_{gro,ALG,To} e^{\beta_{ALG} (T-T_0)} \frac{S_{NH4}+S_{NH3}}{K_{N,ALG}+S_{NH4}+S_{NH3}} \frac{S_{HPO4}+S_{H2PO4}}{K_{HPO4,ALG}+S_{HPO4}+S_{H2PO4}} \frac{I}{K_I} \exp\left(1-\frac{I}{K_I}\right) X_{ALG}$
(9b)	Growth of Algae with NO_3	$k_{gro,ALG,To} e^{\beta_{ALG} (T-T_0)} \frac{K_{N,ALG}}{K_{N,ALG}+S_{NH4}} \frac{S_{NO3}}{K_{N,ALG}+S_{NO3}} \frac{S_{HPO4}+S_{H2PO4}}{K_{HPO4,ALG}+S_{HPO4}+S_{H2PO4}} \frac{I}{K_I} \exp\left(1-\frac{I}{K_I}\right) X_{ALG}$
(10)	Aerobic Respiration of Algae	$k_{resp,ALG,To} e^{\beta_{ALG} (T-T_0)} \frac{S_{O2}}{K_{O2,ALG}+S_{O2}} X_{ALG}$
(11)	Death of Algae	$k_{death,ALG,To} e^{\beta_{ALG} (T-T_0)} X_{ALG}$
(12 a-e)	Growth of Consumers on X_i	$k_{gro,CON,To} e^{\beta_{CON} (T-T_0)} \frac{S_{O2}}{K_{O2,CON}+S_{O2}} X_i X_{CON}$, i = ALG, S, H, N1, N2
(13)	Aerobic Respiration of Consumers	$k_{resp,CON,To} e^{\beta_{CON} (T-T_0)} \frac{S_{O2}}{K_{O2,CON}+S_{O2}} X_{CON}$
(14)	Death of Consumers	$k_{death,CON,To} e^{\beta_{CON} (T-T_0)} X_{CON}$
(15)	Hydrolysis	$k_{hyd,To} e^{\beta_{hyd} (T-T_0)} X_S$
(16)	Eq. CO_2 - HCO_3^-	$k_{eq,1}(S_{CO2} - S_H S_{HCO3} / K_{eq,1})$
(17)	Eq. HCO_3^- - CO_3^{2-}	$k_{eq,2}(S_{HCO3} - S_H S_{CO3} / K_{eq,2})$
(18)	Eq. H^+ - OH^-	$k_{eq,w}(1 - S_H S_{OH} / K_{eq,w})$
(19)	Eq. NH_4^+ - NH_3	$k_{eq,N}(S_{NH4} - S_H S_{NH3} / K_{eq,N})$
(20)	Eq. $H_2PO_4^-$ - HPO_4^{2-}	$k_{eq,P}(S_{H2PO4} - S_H S_{HPO4} / K_{eq,P})$
(21)	Eq. Ca^{2+} - CO_3^{2-}	$k_{eq,s0}(1 - S_{Ca} S_{CO3} / K_{eq,s0})$
(22)	Ads. of Phosphate	$k_{ads} S_{HPO4}$
(23)	Des. of Phosphate	$k_{des} X_P$

Figure 29: Processes and process rates of the RWQM1 model [REICHERT et al., 2001]

Furthermore, it is mentioned that the models from the 'big' software developers for modelling the world of water Danish Hydraulics Institute (DHI; MIKE11, MIKE21, MIKE3), from WL / Delft Hydraulics (SOBEK, DELFT3) and from Sogreah (TELEMAC2D, TELEMAC3D) forsee components for simulating water quality.

Water quality models also require many data which partially can be taken from the literature and partially must be measured for driving, calibrating and validating the models. Some water-quality models for rivers have a certain relation to problems in sewer systems because they also account for some microbial processes which occur in sewers. However, they generally neither focus on the sulphur cycle nor simulate the mass transfer of components (as hydrogen sulphide) from water to gas.

7.5 Integrated models

There are some integrated models which combine parts of urban drainage, wastewater plants and water quality in rivers, for example ERBE (2004), SCHRÖDER et al. (2005) or PETERS (2007). The SIMBA model also belongs to the groups of integrated models as it combines urban drainage (SIMBA Sewer, see sec. 7.2) and wastewater plants (see sec. 7.3) and as it is principally also capable of integrating water quality in rivers.

The foci of the above-mentioned models is generally on integrated studies which concern the optimization of wastewater management, real time control, rainwater harvesting, reduction of outflow from combined sewers or other problems. As they do not treat odour and corrosion in sewers, they are not further commented on, here.

7.6 Flow, transport and reaction models in sewers and the WATS model

As already mentioned, there are only very few models with relation to odour or / and corrosion in sewer systems.

ALMEIDA et al. (1999) developed a tool for the predicting of in-sewer changes in wastewater quality under aerobic conditions focussing on dry weather conditions. They used hydro-numerical models for water flow and advective / dispersive transport, while reactions are based on a concept similar to ASM1. Processes such as reaeration, heterotrophic growths and decay, hydrolysis, ammonification and biofilm consumption of substrate and oxygen are considered. They focussed on sensitivity analyses about the model parameters which indicated that the yield and maximum growth rate of heterotrophs were the most sensitive ones. However, the sulphur cycle was not considered.

HUISMAN (2001) developed a model for transport and transformation processes in combined sewers which has been included into the AQUASIM model. Water flow and transport were modelled with a hydro-numerical approach, reaction processes were based on the ASM3. The main objectives of the work have been biofilm activities and oxygen balances. Sulphur components were included in the model concept, however, their influence was negligible.

7.6.1 WATS model

WATS is the abbreviation of Wastewater Aerobic / anaerobic Transformations in Sewers. It simulates flow, transport as well as microbial and chemical reaction processes in sewer systems. WATS accounts for the water, gas and solid (pipe wall) phase, transformations of organic matter, sulphur and nitrogen as well as mass transfer-processes via the phase interfaces including variable temperature and ph-conditions. The fundamentals of WATS are documented in the book of HVITVED-JACOBSEN (2002) which is based on the lessons learnt and the experiences of the author and his research group gained in more than two decades of work. An overview about the processes involved is given in Figure 30. The WATS model is probably the only one worldwide, which is already capable to simulate odour and corrosion in sewer systems (personal communication with the developers).

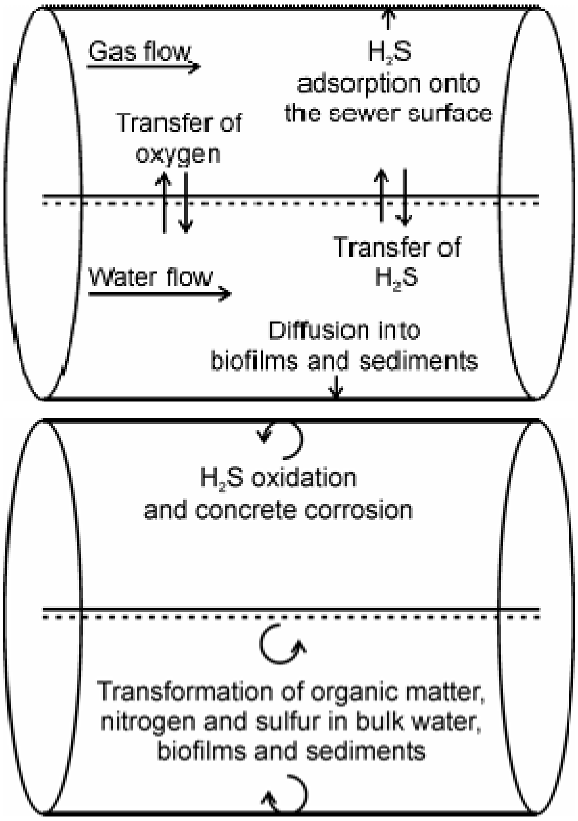


Figure 30: **Flow and mass-transfer processes (left) and transformation processes (right) (taken from: www.sewer.dk)**

As WATS concentrates on dry weather conditions, water and gas flow is just considered in very simple way. The water flow is stationary and uniform based on Manning's friction law. Therefore, several flow processes which can be determined from the solution of the Saint-Venant equations such as non-uniform and instationary flow as well as a turbulence parameterisation are not included, i.e. for example that the simulation of the flow conditions around drops is not possible. However, WATS can be applied to gravity sewers and pressure mains. The gas flow is also assumed to be stationary, i.e. also that non-uniform and instationary flow as well as turbulence are not treated. The gas flow is not computed, it is determined from measurements or estimated to be a certain percentage of the water flow, for example 15%. Therefore, WATS is hardly capable to simulate countermeasure like different ventilation scenarios. A friction condition between the water and gas phase which is common practice in river hydraulics to account for the wind influence on the water flow is not included.

Concerning the transport simulation, diffusion / dispersion is neglected in the water phase. In the gas phase, diffusion / dispersion is also not modelled, but estimated from measurements. Sediment transport, deposition and erosion are also not addressed.

The major emphasis of the WATS model consists of the concept for the microbial and chemical processes of organic matter, sulphur and nitrogen in the water and gas phase as well as the mass transfer processes water-gas and gas-solid (pipe wall) including variable temperature and ph-conditions. An overview is given in Figure 31. The organic matter (measured as the total COD) is subdivided into four components (heterotrophic biomass, readily biodegradable substrate, fast and slow hydrolysable substrates), and three sulphide fractions (dissolved sulphide, particulate sulphide, gaseous hydrogen sulphide) are considered. The kinetics include aerobic and anaerobic transformations of organic matter, hydrogen sulphide formation, sulphide oxidation in water and biofilm, sulphide oxidation in the gas phase / sewer wall (adsorption, corrosion). The mass transfer between the water and gas phase accounts for reaeration and sulphide emission depending on Henry's law. Corrosion rates are described by a Monod-type reaction depending on the hydrogen sulphide concentration in the gas phase. A matrix notation of most of the mentioned reaction processes is shown in Figure 32.

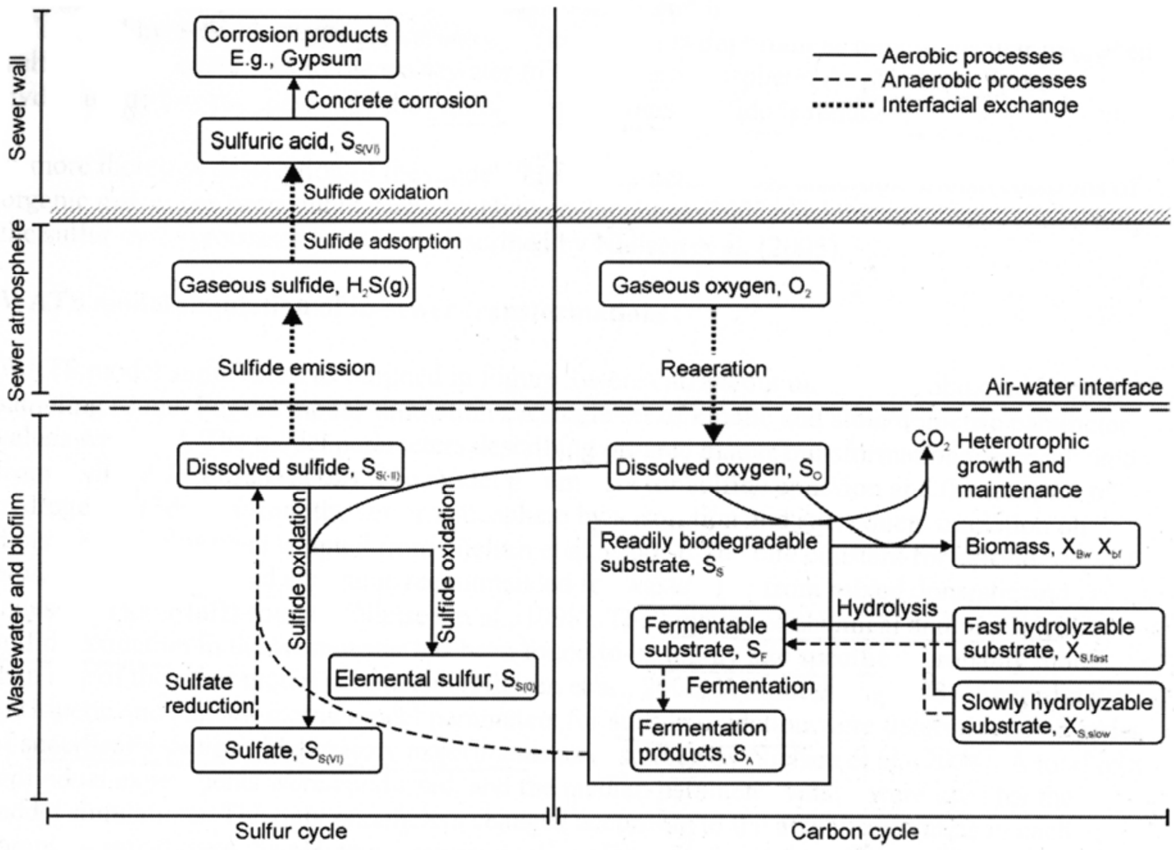
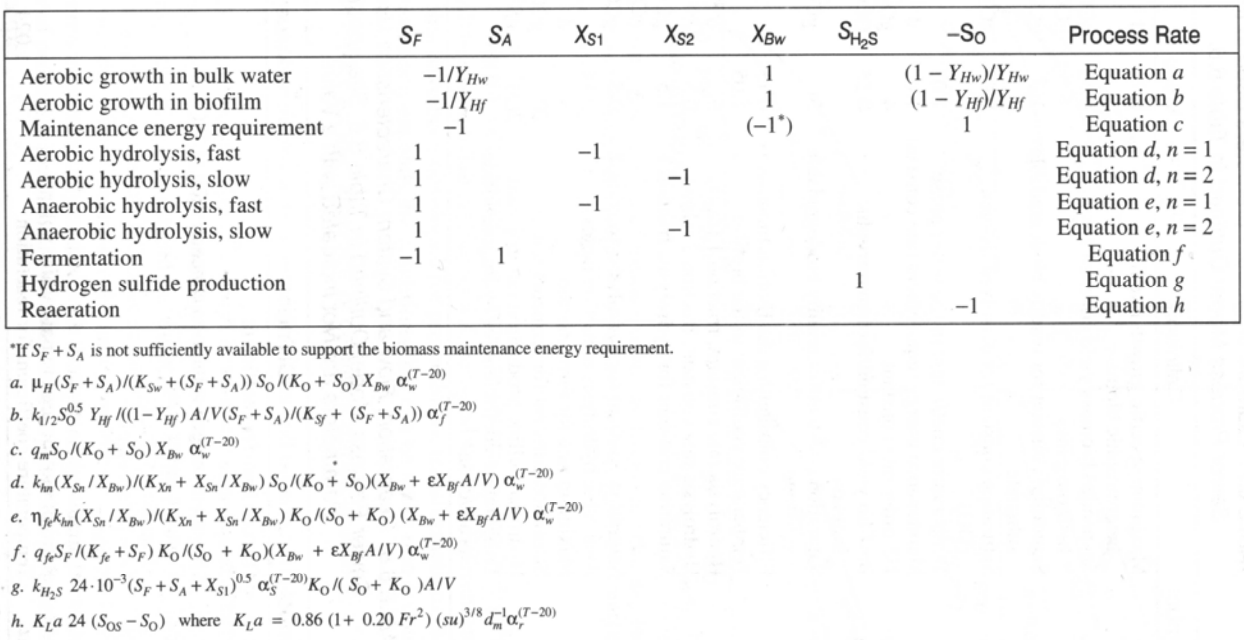


Figure 31: **Model concept for reaction and mass-transfer processes [after NIELSEN et al., 2006]**



	S_F	S_A	X_{S1}	X_{S2}	X_{Bw}	S_{H_2S}	$-S_O$	Process Rate
Aerobic growth in bulk water	$-1/Y_{Hw}$				1		$(1-Y_{Hw})/Y_{Hw}$	Equation *a*
Aerobic growth in biofilm	$-1/Y_{Hf}$				1		$(1-Y_{Hf})/Y_{Hf}$	Equation *b*
Maintenance energy requirement	−1				(−1*)		1	Equation *c*
Aerobic hydrolysis, fast	1		−1					Equation *d*, $n = 1$
Aerobic hydrolysis, slow	1			−1				Equation *d*, $n = 2$
Anaerobic hydrolysis, fast	1		−1					Equation *e*, $n = 1$
Anaerobic hydrolysis, slow	1			−1				Equation *e*, $n = 2$
Fermentation	−1	1						Equation *f*
Hydrogen sulfide production						1		Equation *g*
Reaeration							−1	Equation *h*

*If $S_F + S_A$ is not sufficiently available to support the biomass maintenance energy requirement.

a. $\mu_H(S_F+S_A)/(K_{Sw}+(S_F+S_A))\ S_O/(K_O+S_O)\ X_{Bw}\ \alpha_w^{(T-20)}$

b. $k_{1/2}S_O^{0.5}\ Y_{Hf}/((1-Y_{Hf})\ A/V(S_F+S_A)/(K_{Sf}+(S_F+S_A))\ \alpha_f^{(T-20)}$

c. $q_m S_O/(K_O+S_O)\ X_{Bw}\ \alpha_w^{(T-20)}$

d. $k_{hn}(X_{Sn}/X_{Bw})/(K_{Xn}+X_{Sn}/X_{Bw})\ S_O/(K_O+S_O)(X_{Bw}+\varepsilon X_{Bf}A/V)\ \alpha_w^{(T-20)}$

e. $\eta_{fe}k_{hn}(X_{Sn}/X_{Bw})/(K_{Xn}+X_{Sn}/X_{Bw})\ K_O/(S_O+K_O)\ (X_{Bw}+\varepsilon X_{Bf}A/V)\ \alpha_w^{(T-20)}$

f. $q_{fe}S_F/(K_{fe}+S_F)\ K_O/(S_O+K_O)(X_{Bw}+\varepsilon X_{Bf}A/V)\ \alpha_w^{(T-20)}$

g. $k_{H_2S}\ 24\cdot 10^{-3}(S_F+S_A+X_{S1})^{0.5}\ \alpha_S^{(T-20)}K_O/(S_O+K_O)A/V$

h. $K_La\ 24\ (S_{OS}-S_O)$ where $K_La = 0.86\ (1+0.20\ Fr^2)\ (su)^{3/8}d_m^{-1}\alpha_r^{(T-20)}$

Figure 32: **Matrix notation for the reaction processes [HVITVED-JACOBSEN, 2002]**

The processes in biofilms are very complex and a field of science for itself. An overview about biofilm kinetics is found in HARREMOËS (1978), HENZE et al. (1995), LOHSE (1986) and BROCKMANN (2006). For odour and corrosion in sewers, 'simpler' expressions are required. Fick's second law of diffusion and a Michaelis-Menten (Monod) kinetic are used to describe the transport and transformation processes in the biofilm. The aerobic biofilm growth is approximated with a half order kinetic. Biofilms in the gas phase are not (directly) accounted for. Indirectly, the biofilms in the gas phase have an influence on the adsorption and corrosion rates which depend on the ph and temperature conditions.

Additonally to the book of HVITVED-JACOBSEN (2002), other literature of his group is worth to be mentioned and contains newer results compared to 2002. Overall, the studies of this group resulted in more than 150 publications. In HVITVED-JACOBSEN (1998) the process and model concept for microbial wastewater transformations in gravity sewers is explained much briefer compared to the book. HVITVED-JACOBSEN & VOLLERTSEN (2001) introduce the formation of hydrogen sulphide and odourous substances in wastewater also much briefer compared to the book. NIELSEN et al. (2005) present simulations of sulphide buildup in wastewater and atmosphere of sewer networks. This paper has a special focus on the sulphur cycle in water, gas and the sewer wall, and it has implemented the corrosion rates from ESOY et al. (2002). In that context, the corrosion rates determined by WEISSENBERGER (2002) are also mentioned (also WEISSENBERGER does not belong to the group of HVITVED-JACOBSEN). VOLLERTSEN et al. (2005) introduce a stochastic approach to account for parameter uncertainties and parameter sensitivities. MADSEN et al. (2006) specially focus on gas-phase transport and ventilation. NIELSEN et al. (2006) present a field study and simulations about aerobic and anaerobic transformations of sulphide in a sewer system.

No model output can be better than the model input! Data stem from measurements, the literature, experiences and model calibration. For example, the wastewater characteristics are a very important input parameter. The group of HVITVED-JACOBSEN has published many data in the above-mentioned more than 150 publications. This can serve as a good starting condition for our planned project or other groups which will simulate odour and corrosion. A number of parameters is very site-specific and must be determined by model calibration, i.e. by a best fít of measurements and computations. Stochastic methods are used to determine the parameter sensitivity and to decide which parameter must be measured or calibrated and which parameter can be chosen from the literature or experiences.

The numerical solution of the coupled non-linear differential equations is based on the FDM. Therefore, there is room for numerical improvements, for example using the FVM. It is obvious that the parameter uncertainties are much more important here compared to ‘highly’ developed numerics, nevertheless state of the art numerics should be applied. Furthermore, the software design can be improved, for example using object-orientated methods.

7.6.2 Conditions for odour and corrosion

In gravity sewers, high temperature, low flow velocities and stagnant wastewater, high turbulence and stripping of hydrogen sulphide, large water depths, large biofilm to water ratio, high COD concentrations and sediment deposits increase the risk for odour and corrosion. When wastewater is transported in pressure mains, anaerobic conditions rapidly will develop as no reaeration takes place. Even at low temperatures, significant hydrogen sulphide will be produced at typical transport times and COD concentrations. Downstream of the pressure main outlets, hydrogen sulphide is stripped out, especially under highly turbulent conditions.

7.7 Conclusions, deficits and research experiences

Empirical formulas are just capable of giving a very rough estimation of the sulphide development in sewers and they are poorly transferable to general conditions. Urban drainage, wastewater plant and water quality models have some more or less close relations to the simulation of flow, transport and reactions processes in sewers systems. Among, the very few models which are capable to simulate the above-mentioned processes, only the WATS model has been applied to odour and corrosion problems in sewer systems.

The WATS model has its strength in simulating the microbial and chemical reaction processes of organic matter, sulphur and other components in the water and gas phase including mass transfer water-gas and corrosion with a focus on dry weather conditions. Current deficits of WATS are in the flow simulation (no non-uniform and instationary water flow, no turbulence, no gas flow) and the transport simulation (no diffusion / dispersion in water and gas, no sediments and erosion / deposition). Problems dealing for example with rainwater conditions, ventilation, flushing, flow over drops can not be treated with WATS. Furthermore, the numerics and the software design can be improved. The WATS model is not public domain, and the sources and the software are not available. However, the developers are very open for collaborations (personal communication). The amount of the source code is not very high and all methods are published. The quality of the WATS model strongly relies on the availability and quality of data, and many data of the WATS group are published, too.

The author Hinkelmann has more than 15 years research experiences in the fields of the development and application of models for simulating flow, transport and reaction processes in subsurface (groundwater, water-gas flow) and free-surface flow systems (rivers, estuaries) as well as in the fields of integrated models and hydroinformatics. His experiences are summarized in the book ‘Efficient Numerical Methods and Information-Processing Techniques for Modeling Hydro- and Environmental Systems’ published by Springer in 2005. Since 2004, he is head of the Department of Water Resources Management and Modeling of Hydrosystems at the Technische Universität Berlin. Current research projects and publications are found at www.wahyd.tu-berlin.de.

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