4 Biological and Bio-Mechanical Processes

Contributions by Konrad Soyez, Sebastian Plickert, Konrad Schleiss, Saburo Matsui, and Helmut Brandl

Robert F. Curl, Nobel Prize winning chemist, stated in 1996 that *"this was the century of physics and chemistry, but it is clear that the next century will be the century of biology."* Great advances are expected from a better understanding and control of biological processes, and raise the question of whether biotechnology will be the preferred technology for solving environmental problems in the future.

The trick to applying biological processes in waste treatment is to exploit the large potential of microorganisms for efficiently transforming organic and inorganic constituents in a way that avoids harmful emissions to the environment. Environmental biotechnology includes air pollution control, waste-water treatment, soil remediation, and groundwater clean-up as well as waste treatment. In the course of a recent conference it was argued that "*process-integrated biotechnology plays an important role in reducing environmental damage as well as cost reduction.*" Process-integrated biotechnology is characterized by the application of biocatalysts (enzymes, microorganisms) in an industrial process and the substitution of existing processes or the development of entirely novel processes. These concepts can also be applied for novel municipal solid waste management systems: Mechanical-biological waste pretreatment is an example of such a technique and is currently applied in Germany. The pretreatment combines mechanical treatment (shredding, sieving, sorting) and aerobic composting as well as anaerobic fermentation. As a result, MSW is stabilized and the hazardous potential of the waste is reduced. Natural biological processes occurring in any waste dump (e.g. the degradation of organic matter) are “domesticated” and integrated into an industrial process. Usually, these techniques do not apply genetically modified microorganisms, but rather stimulate naturally-occurring microbial populations in the respective ecosystems. In addition to the biological treatment of MSW fractions rich in organic matter, the metal-containing MSW fractions can also be subjected to a biological treatment. This is particularly the case for fly and bottom ashes resulting from MSW incineration. Ideally, metals can be recovered and re-used in metal-manufacturing industries. Biological processes can also be integrated into landfill management. Novel approaches of landfill techniques mainly include odor control measures and enhanced landfill stabilization by the selective inhibition or stimulation of the present microflora. These methods have the potential to improve landfill techniques in developing countries as well.

Because they are based on the natural biogeochemical elemental cycles, biological processes have a great potential to contribute to the development of future sustainable MSW treatment technologies. It is also a fact that biological techniques are highly accepted by the public, suggesting a natural method of solving environmental problems.

Biological techniques have some advantages in comparison to chemical or physical methods applied in MSW treatment: i) as previously mentioned, microorganisms act as natural biocatalysts; ii) biologically-based techniques are characterized by low hazardous emissions; and iii) are generally considered as “low-tech” and therefore “low-cost” systems. However, biological treatment technologies reveal certain disadvantages as well: i) biological processes are susceptible to changes in process conditions such as differences in available oxygen, pH, or temperature and therefore need balanced process control; ii) biological systems have only a limited tolerance towards toxic compounds; and iii) most important, often require very long residence times and, therefore, large reaction volumes.

Waste treatment is not a process which creates large added value, and the economic boundary conditions thus limit the feasibility of many new technical solutions. Clever combinations of physico-chemical and biological processes exploiting the specific advantages of both types of technology seem to be most promising for the time being. Biological science and technology are expected to advance dramatically in the coming century, as the above citation and many others suggest, and it is very likely that these developments will shape the environmental technology of the 21st century.

4.1 Mechanical-Biological Treatment of Waste (MBP)

Konrad Soyez and Sebastian Plickert

Mechanical-biological treatment of municipal solid waste (MBP) is defined as the processing or conversion of waste from human settlements (households, etc.), which include biologically degradable components, by a combination of mechanical processes (e. g. crushing, sorting, screening) and biological processes (aerobic "rotting", anaerobic fermentation) [1].

At the beginning of the development of MBP, it was applied as a pre-treatment technology for residual waste before landfill (hence the common abbreviation "MBP"). It aimed primarily at the reduction of the mass, volume, toxicity and biological reactivity of the waste, in order to minimise environmental impacts from waste deposition such as landfill gas and leachate emissions as well as settlements of the landfill body. Concerning these points, MBP competed with waste incineration. The recovery of reusable waste components such as metals and plastics, then, was only an incidental to the minimization of the waste amounts. In recent years, the recovery of waste components for industrial re-use has become an integral part in the development of MBP, especially concerning the production of refuse derived fuels (RDF). Thus, MBP is now an integrated technology for the material flow management of MSW, where almost half of the input flow is recovered for industrial re-use, and only one third remains for deposition (Fig. 4.1). A further 20% are process losses in the biological stage, converted into biogas in the case of an anaerobic process.

The mechanical-biological treatment of municipal solid waste has been applied for approximately ten years, specifically in Germany, Austria and Switzerland on technical scale, but also in several developing and emerging countries on a pilot plant scale. In Germany about 1.8 million tons of MSW are treated in 29 mechanical-biological pre-treatment plants [2], compared to twelve million tons treated by incineration in 51 facilities.

Since March 1st 2001, the application of MBP in Germany has been ruled by the German Ordinance on Environmentally Compatible Storage of Waste from Human Settlements (Abfallablagerungsverordnung, AbfAblV) [1]. It defines quality limits for the pre-treated waste, e.g. limit values for heavy metals, AOX and the reactive organics. Standards for the process emissions are defined by the 30th Ordinance on Execution of the Federal Immission Control Act: Ordinance on Facilities for Biological Treatment of Waste (30. BImSchV). For material flow management, required limit values are defined for TOC and the upper thermal value of the output material for deposition (18% resp. 6000 kJ/kg). To meet these requirements, all MBP facilities in Germany have to separate out a considerable fraction of high calorific waste components, which is then predominantly utilized as RDF. Thus, the new ordinances support the development of MBP from a waste disposal technology towards a technology for material flow management.

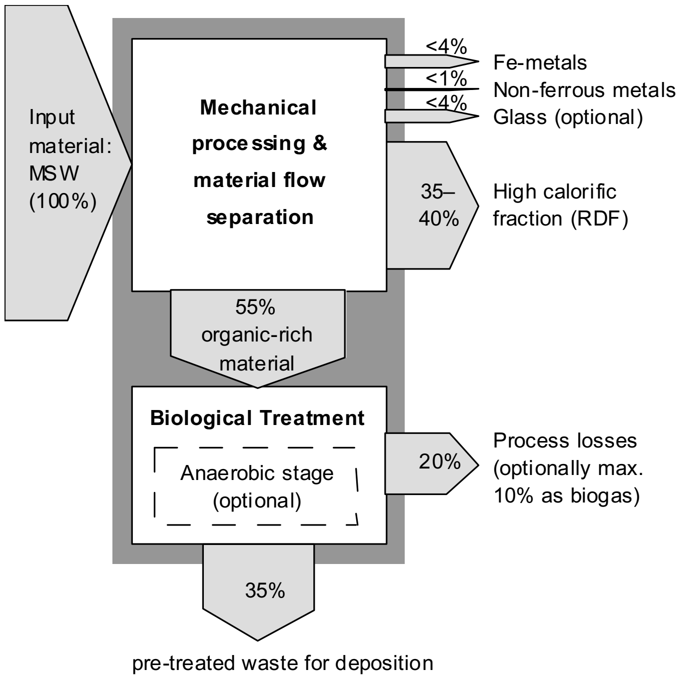

Fig. 4.1. Principal material flow diagram of a MBP plant

For this aim, MBP comprises several mechanical and biological process steps and combinations thereof. The mechanical step is important for the pre-processing of the material before the biological step, but its main task is the separation of the material streams. The biological step mostly determines the residual organic content and thus the landfill behaviour, but may also influence the separation behaviour of the material. Hence, there is not necessarily a strict sequence between the mechanical and the biological stage. Part of the mechanical processing may take place after or even within the biological step, e.g. the separation of metals from the output material or the removal of heavy, mineral-like substances at the bottom of a biogas reactor.

4.1.1 Separation of Organic and RDF Fractions by Mechanical Processing

In general, the mechanical processing inside an MBP plant has the following functions:

1. Removal of contaminants and components which impede the mechanical or biological processes;
2. Adjustment of the particle size distribution for the subsequent processes;

3. Recovery of waste components, such as ferrous and non-ferrous metals, optionally glass and plastics, for recycling;
4. Recovery and processing of a high calorific fraction destined for energy recovery as refuse derived fuel (RDF);
5. Pre-processing of the remaining material for biological treatment, e.g. homogenisation and adjustment of the material's water content.

To fulfil these tasks, a combination of various mechanical processing devices is applied in MBP plants, mainly crushing and screening units, which are also used in traditional waste processing [53]. There is still substantial potential for the optimisation of mechanical units used for MBP.

As MSW is a very inhomogeneous and complex mixture of both organic-rich, high calorific, metal and mineral-like components, the separation of material fractions is generally not suited to compromise concerning decisions between maximum output flows and high product qualities. Thus, an optimisation has to be made for each mechanical step, according to the individual waste composition and the quality demands for the products recovered.

The separation of high-calorific or organic-rich fractions is even more complicated, because neither the calorific value nor the organic content is a suitable property for material separation (in contrary, e.g. to magnetism, which is an unique property in the separation of ferrous metals). Thus, only secondary material properties such as particle size and density or a varied crushing behaviour can be used for physical separation, but this causes a low selectivity. In addition to this, the separation effect of technical screening units is significantly worse than in laboratory, especially when the throughput is close to the machine's capacity [22].

Another compromise situation can be seen in the fact that the organic-rich components also contribute to the waste's calorific value. Hence a maximum output of the energy content, on one hand, and a maximum organic load in the remaining material on the other, are also conflicting goals. As the purpose of the biological treatment is to reduce the input of reactive organics into the landfill, the organic load of this fraction must not necessarily be maximized. However, the portion of total organic load in the remaining fraction also has to be taken into consideration to ensure an optimal material flow separation.

4.1.2 Case Study: RDF Separation by a Two-Step Mechanical Process

Figure 4.2 exemplifies a compromise situation, like the one described above, for a simple two-step mechanical separation of RDF from the input material for the biological step in the MBP plant in Quarzbichl, Germany [22]. In this case, a compromise has to be found for the conflicting goals of a) a maximum transfer of the waste's energy content into the coarse-grained fraction for energy recovery, and b) a maximum calorific value of this fraction.

In Figure 4.2, the assumed quality demand for RDF, due to market reasons, has a calorific value of 15´000 kJ/kg (see vertical broken line; the minimum for energy recovery according to German law is 11´000). As no screen fraction of the non-crushed material reaches this value (see the graph on the left), crushing the waste is indispensable to the production of RDF. The highest calorific values are reached by the hammer mill or the roll crusher, when screened at 150 mm (points 'A' and 'B'). In order to choose an optimally suitable crushing device, the portion of total energy in the RDF output has to be considered: At the points 'A' and 'B', only 7% resp. 16% of the waste's total energy is recovered. When crushed by a revolving composting drum, the portion of total energy in the RDF output rises to 31% at 80 mm screen overflow (point 'C'). The 40 mm screen overflow (point 'D') contains 48%, while its calorific value is only slightly below 15´000 kJ/kg.

Concerning the organic load in the remaining fraction, the combination of a revolving composting drum and a 40 mm screening device is equally acceptable, as it almost doubles the organic load in the 40 mm screen underflow compared to non-crushed MSW (determined as organic dry matter of biological origin). Only the hammermill crusher reaches higher accumulation of reactive organics in the underflow, but the difference in the 40 mm screen underflow is negligible compared to the sizable difference in the RDF output (see above).

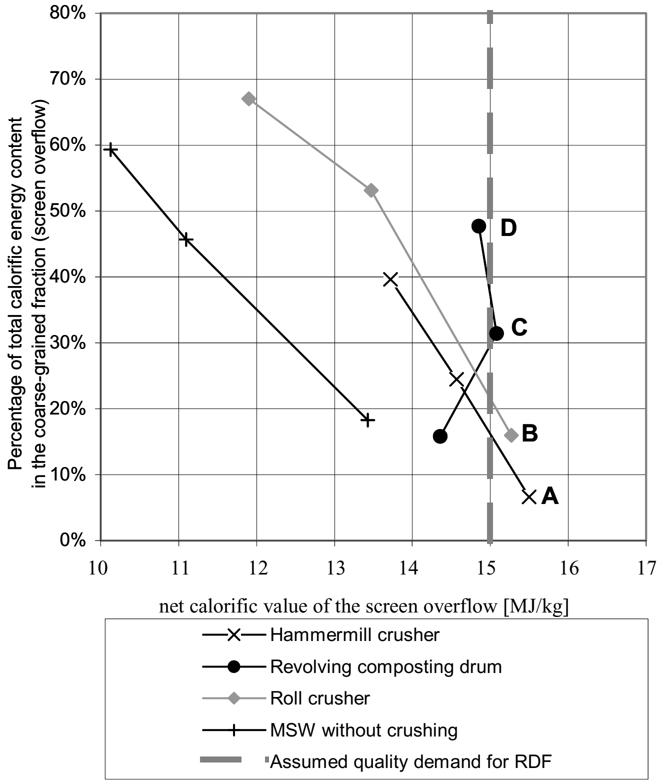

Fig. 4.2. Effects of different crushing devices and screening sizes on the calorific value of the screen overflow and on the total calorific energy recovered as RDF (the 3 data points on each graph represent – from top to bottom – the screen overflows at 40, 80 and 150 mm)

Under real conditions, the demands on both product and separation quality are more critical, thus requiring a more sophisticated system for mechanical processing and separation. Naturally, the optimisation of such a complex system is much more demanding than the example given here, especially as the process expenditures also have to be considered, both economically and ecologically.

4.1.3 Improved Material Flows by the ‘Dry Stabilate’ Process

Another approach to material flow management by mechanical-biological processes is the ‘dry stabilate’ process developed by the Herhof Company [48], applied in four facilities in Germany with a capacity of 75’000 to 180,000 tons each. The goal of this process is to make a maximum percentage of waste available for industrial re-use, thus minimizing the amounts for deposition.

To achieve this, the entire waste is brought into the biological stage, where it is dried using physical and biological processes for 7 days under high aeration rates. Within this process, the organic content is reduced only slightly, and the separation behaviour is improved significantly. This is followed by a separation into a heavy and a light fraction. The light fraction is used as RDF after a further separation of metals. The heavy fraction (about 15 %) is separated into metals, glasses, batteries, and mineral components.

Table 4.1 shows that in this process more than two thirds of the input flow are recovered for industrial re-use, while only 4% remains for waste disposal, i.e. waste incineration. The rest is lost in the process and stripped out with the process air, which is purified by a sophisticated regenerative incineration technology.

Table 4.1. Output flows of the ‘dry stabilate’ process [48]

Output fractions	% of total input
Fractions for industrial re-use:	
RDF (calorific value: 15–18 MJ/kg)	53
Ferrous metals	4
Non-ferrous metals	1
Batteries	0,05
White glass	3
Brown glass	0,5
Green glass	0,5
Minerals	4
Total	66,05
Others:	
Fine grain and dust.	4

4.1.4 Biological Processing and Effects on Landfill Characters

Technical Performance

The aim of the biological stage of a regular MBP plant is to reduce the content of organic material to form a low-reactive "stabilised" product for deposition. The techniques applied are aerobic rotting, anaerobic fermentation, or combinations thereof. Aerobic systems are in widespread use. They include windrows with or without aeration, containers or boxes, drums, and tunnels. Aerobic treatment shows wide variation in both process intensities and duration. Low-tech windrow systems operated directly on the landfill site require only a minimal technical outlay. They can be aerated through drainage pipes which act as vents; the required process time varies from 5 to 15 months (Fig. 4.3).

The majority of contemporary plants include an encapsulated, controlled, intensive biological treatment of 4 to 8 weeks, followed by an extensive maturation process in an open windrow without forced aeration. Actual aeration rates are between 3000 and 8000 m^3/ton waste, while the oxygen needed for the biological process itself is only 2000 m^3/ton in the case of a typical residual MSW and a 60% degradation of the reactive organics.

The new parameters AT_4 and GB_{21} have been introduced as indicators for waste stabilisation in the case of biological waste treatment. They are applied as a substitute to the ignition loss, which is used as an integral criterien for mineralisation by incineration. The GB_{21} indicates the experimental gas formation within 21 days. Alternatively, the respiration coefficient AT_4 is used, and is

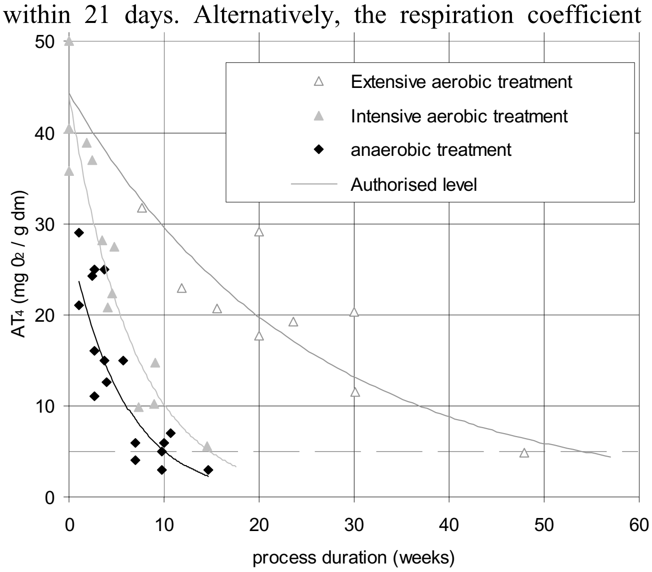

Fig. 4.3. Stability parameter AT_4 as a function of the treatment duration [52]

defined as the amount of oxygen consumed in 96 hours in microbial processes for a specified experimental device [4]. AT_4 is most easily determined: it is preferred for practical process control. For untreated material, typical values of AT_4 are in the range of 40 to 50 mg O_2 per g of dry matter. A sufficient biological treatment results in an AT_4 value of less than 5 mg O_2 per g of dry matter, and in a GB_{21} < 20 l/kg. Figure 4.3 illustrates the process duration required to reach a given AT_4-value dependant upon the intensity of the biological process applied.

Deposition Behavior of MBP Output

The level of contaminants in both leachate and gas emissions of the treated residual waste is reduced by more than 98% in comparison to untreated waste. One kilogram of treated waste potentially releases a total load of 1-3 g COD, 0.5-1.5 g TOC, and 0.1-0.2 g NH_4-N into the leachates. The real numbers clearly depend on the intensity resp. the duration of the pre-treatment (see Table 4.2 for leachate concentrations)

Table 4.2. Leachate parameters as functions of the process duration in windrows [13]

Parameter	Process duration [months]			
	3	6	9	13
COD [mg/l]	701	425	320	215
BOD_5 [mg/l]	46	4.6	4.3	3
TOC [mg/l]	328	174	128	80
NH_4-N [mg/l]	20	10	3.7	1

The waste treated can be compacted in the landfill to a density of 1.5 tons/m^3 (wet). This leads to a better use of landfill capacity. The hydraulic conductivity (k_f-value) is approximately $k_f = 10^{-8}$ m/s or even lower. Water flow through the landfill is therefore partly prevented, and the leachate volume decreases considerably.

To achieve these effects, the landfill construction is to be optimised according to the conditions determined by the waste, the shape of the landfill surface, the area open for the material input, etc. A special aspect is the very low level of remaining gas production, especially methane, which at a maximum is less than 1 l CH_4/m^2*h [18]. On this level, no active landfill gas collection is possible. To reduce the remaining emissions to an environmentally acceptable minimum, a passive oxidation is applied by a bio-active oxidising landfill cover.

MBP Emissions and Cleaning Technologies

The emissions from the biological pre-treatment process are the following:

1. Carbon dioxide and methane produced by aerobic resp. anaerobic biological activities;
2. Organic compounds metabolised or generated by biological reactions;
3. Volatile substances stripped out from the original waste;

4. Heavy metals and heavily volatile substances which mostly remain in the residues;
5. Germs, as bacteria and moulds, emitted from the system as a result of the bioprocess.

The total organic compounds emitted amount to 600 g per ton of original material, measured as non-methane volatile organic compounds (NMVOC). Methane may amount to approximately 100 g per ton of original waste, or even more in the case of difficulties in the process. Ammonia amounts to about 500 g per ton of original waste. In the bio-filter it can be transformed into N_2O, which is a climate relevant gas [15].

To avoid health and climate risks from the emissions, the waste gas is collected and cleaned during this period. Scrubbers and bio-filters are traditionally used. They achieve a mean reduction by 50%, so that about 300 g TOC per ton of waste remain [15], including difficult to degrade chlorinated carbohydrates. Further detoxification by an extra thermal process has to be applied in order to reach the exact TOC limit value of 55 g/Mg, which is analogous to the limit in the case of waste incineration.

Evaluation of the Technology, Future Trends and Research Needs

By producting components for industrial re-use, MBP contributes directly to an improved resource management. The future development of the MBP technology will strongly depend upon successes in the marketing of the products. The most important fraction is the RDF, which can be used as a substitute for fossil fuels, but also as a raw material for synthesis gases in the chemical industry or even for hydrogen as an energy source. To broaden the applicability of RDF, a standardisation of the product quality and a stable high quality production is necessary. In Germany, a quality certificate (RAL-GZ 724) was introduced in 2001 [21].

Future improvements for high standard MBP can be seen in an integrated design of the MBP plants with particular respect to the waste composition, infrastructure and ecological situation. Potential combinations with existing waste management facilities, such as incineration plants and landfills, have to be considered. The design process must be adapted to market demands concerning the amount and the quality of recycling products.

With respect to the realisation of the technology itself, air flow management inside the plant is of major interest. The air flows have to be reduced by closing loops and implementing a specific treatment of waste air streams according to their individual qualities. However, for the waste gas of the intensive biological step, a thermal treatment is imperative. The mechanical separation processes must be improved by defining clear separation goals, according to which an appropriate machinery has to be developed.

With respect to waste deposition, MBP technology has some benefits in comparison to other treatment options. In the case of poor management of landfills or a low availability of suitable grounds, MBP can contribute to a rapid improvement of the waste management situation, with respect to landfill gas production, leachate emissions, and settlements. One advantage is a higher flexibility in comparison to incineration. It can be easily adapted to changes in waste volume or composition. Thus, it seems well suited to the situations in many developing and emerging countries as a first step toward an effective waste management. Under higher developed waste management conditions, MBP has to compete with other options of waste management according to ecological and economical preferences. Ecologically, MBP has advantages with respect to risks to human health, but disadvantages in climate effects. Typical costs of a high-tech MBP are in the range of 80 to 100 € per ton, which corresponds to the lower range of incineration. The minimum capacity for an economical operation of MBP facilities is between 50.000 and 80.000 tons p.a.

4.2 Composting and Anaerobic Digestion

Konrad Schleiss

Composting is the oldest form of recycling and has long been used to treat waste. In the last century, municipal solid waste (MSW) was composted in many places. Over the last decades, some countries have shifted to separately collected green waste, so as to ensure a marketable quality of the produce. This tendency was particularly marked in Germany, Holland, Austria and Switzerland, where the agricultural use of compost from MSW is forbidden since 1986 [11]. In many countries, composting is still considered a treatment process for municipal waste prior to landfilling.

The processes described here do not apply to neighbourhood- or home-composting initiatives, but above all to facilities treating more than 1'000 tons annually. For marketing reasons, the author considers that only separately treated green waste has a future. Biological treatment before landfilling has other types of requirements than the composting discussed here.

Composting techniques evolved from open-air composting, often plagued by odour problems, to covered composting to anaerobic digestion. Anaerobic digestion, which proceeds in the absence of air, has shown to be particularly suited to water-rich, easily degradable wastes. It therefore complements aerobic composting, where problems were often encountered to aerate poorly structured materials. Anaerobic digestion is a globally isothermic biological process, so requires a good heating for the thermophilic variant, while aerobic composting is highly exothermic, releasing large amounts of heat and is therefore a self-heating process.

The types of waste most adapted to anaerobic digestion or composting are schematically presented in Figure 4.4. This classification is only valid for the dominant waste type of a mixture. For the minor components it is not relevant.

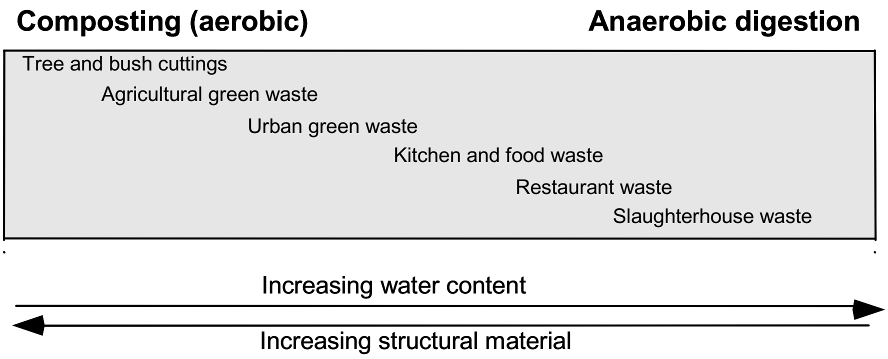

Fig. 4.4. Suitability for aerobic or anaerobic processes [29]

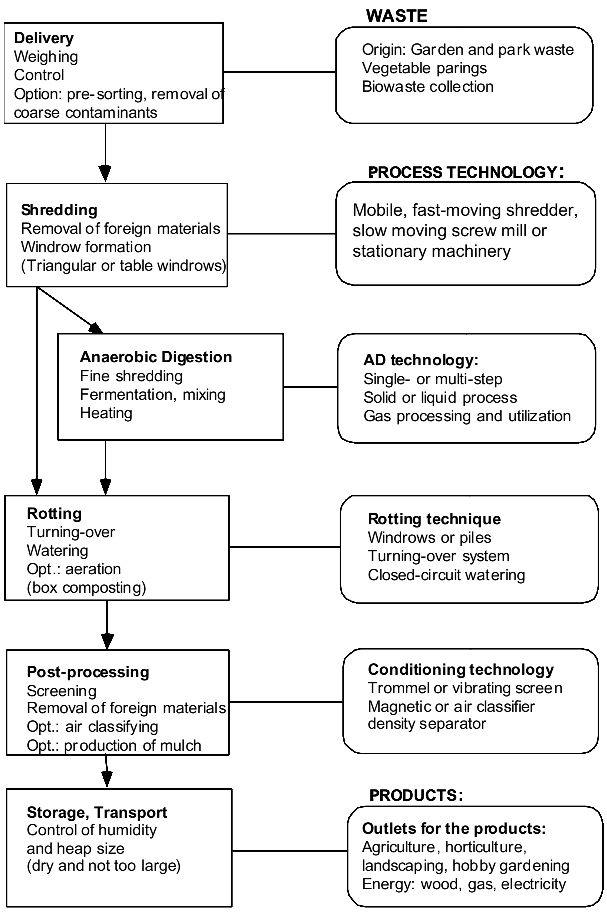

Fig. 4.5: Sequence of operations in a composting or anaerobic digestion facility [23]

Green waste processing has three main aims: to favour the biological processes, to improve the quality of the produce and to ensure operational efficiency. This also includes a regular control of the sanitary harmlessness of the produce (no germinating weed seeds and disease supressivity).

Figure 4.5 shows the sequence of steps required for composting or anaerobic digestion. When processing green waste in centralised facilities, a general requirement is the setting up of corresponding efficient collection logistics. The single treatment steps are described in the following paragraphs.

During *delivery and weighing* the compostability of the waste received is checked. Quality compost requires that the larger contaminants be removed. Weighing the waste is essential for waste management planning and correct billing of the amounts received. *Shredding* is the preparatory step for biological degradation. It must be adapted to the structure of the material, so as to allow for adequate oxygenation: neither too fine (powder), nor too coarse (sticks will favour air bypass). Fine shredding is a prerequisite for efficient degradation in anaerobic digestion. *Anaerobic digestion* (AD) is best for easily degradable materials, that may produce offensive odours if they are composted. AD is also a source of renewable energy. In general the material is shredded a second time in a rotary shredder and the substrate is made into a pulp. As AD is mainly a biological degradation process, a post-maturation phase is necessary to produce compost. The *rotting process* (including turning-over, aeration and watering) is the next step. The turning-over influences the biological process most. Its finality is the mixing, aeration, and watering of the substrate, and these must be carefully balanced one against the other. Turning-over may be partially, but not completely, replaced by forced aeration, as the turning-over mixes the dryer and wetter parts, thus optimising the water balance. *Post-processing and conditioning* consists mostly of culling out the foreign materials and calibrating the product to the required particle size. This is generally carried out after the rotting phase is over. Sometimes mature compost is also stored as is, and only conditioned shortly before sale. In general screens are used to remove foreign materials.

Separately collected biowaste can be divided into garden and park waste and household biowaste (vegetable and kitchen waste). The amounts collected vary greatly depending on the type of settlement and the collection logistics, ranging between 50 and 150 kg per inhabitant per year. In Switzerland, nearly 100 kg per inhabitant of separately collected biowaste are composted or digested each year. Of this, over half comes from municipal collections. The rest stem from gardening and landscaping (Fig. 4.6). Obviously, these materials cannot be reused on-site and are therefore handed over for another use to composting or digestion facilities.

4.2.1 Overview of the Various Processes

Two-thirds of the biowaste is composted in traditional open-air windrows. This technique is characterised by relatively low investment costs and the generally high quality of the product. Its drawbacks are the emission of odours, when too much unsuitable materials are processed (kitchen wastes, etc.), or when the facility

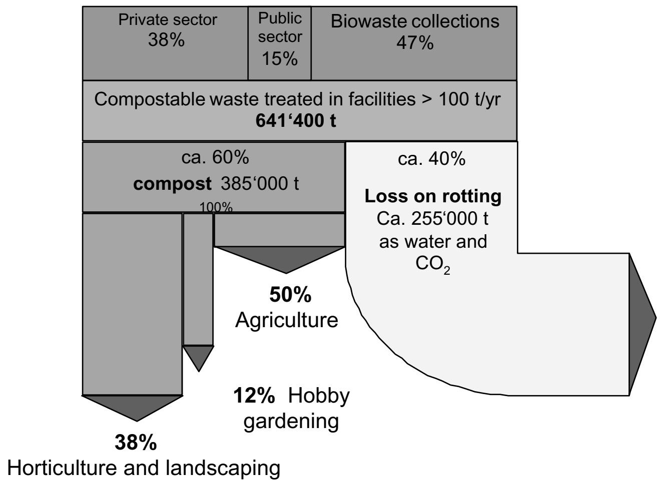

Fig. 4.6. Origin of biowaste and destination of compost in Switzerland in 2000 [12]

exceeds a certain size (5'000 to 10'000 t/yr). Field-edge composting counts as windrow composting, since piles are made along fields, though the amounts treated rarely exceed 1'000 t/yr.

Hall and box composting can be grouped under the heading of covered systems. Covering the facility avoids waterlogging by rainfall. By completely housing a plant, it becomes possible to treat the exhaust air through a biofilter. In Switzerland, only a few plants are completely covered. In Germany, Holland and Austria, this type of plant is more common for large facilities (> 20'000 t/yr). The energy consumption of fully housed facilities, for the forced aeration of the windrows and the air cleansing system, is very high.

In Germany and Switzerland, some 10 to 12 % of the total biowaste is processed by anaerobic digestion (Fig. 4.7). In the canton of Zurich, a pioneer in the field, this percentage rises to over 25 %. With such a ratio, the energy balance of the total collection and processing is positive: biogas production are about double the consumption of diesel fuel by the composting facilities.

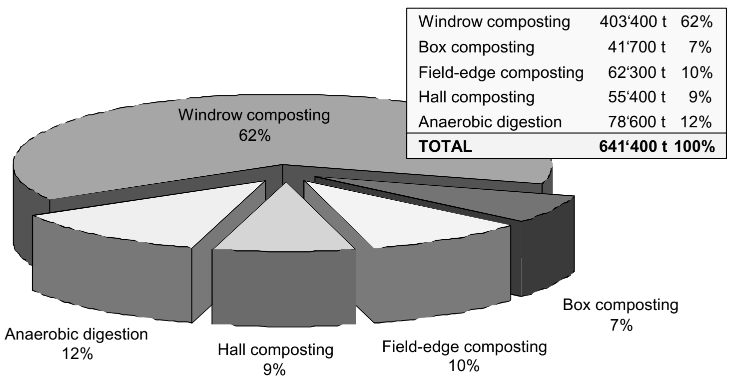

Fig. 4.7. Types of processes used in Switzerland for the year 2000

Table 4.3. Net energy balance (energy production minus energy consumption) of the various biowaste treatment processes

Useful residual energy [kWh/ton]	Electricity	Heat	Fuel	**Total**
AD (100 % electricity production)	130	* 320	0	450
AD (100 % fuel production)	-120	-100	600	380
AD combined heat and power (50/50)	5	* 110	300	415
Wood chips heating	0	1000	-25	975
Composting, open system	0	0	-30	-30
Composting, housed system	-100	0	-20	-120

* Up till now the heat could practically not be used, since most industrial buildings are already equipped with an individual heating system. Therefore, the values for electricity and fuel are most significant.

AD produces on average 100 m^3 of biogas, with a methane content of about 65 %, 34 % carbon dioxide and 1 % trace gases. The energy content amounts to about 6 kWh per m^3 biogas. This gas can be transformed into about 130 kWh electricity by a block heating and generation plant (see Table 4.3). If all the biogas is used as biofuel, 120 kWh electricity are consumed, as well as some heat for the fermentation tank. Optimization is possible with combined heat and power generation.

4.2.2 Prospects: What Should be Improved for a Sustainable Development?

Techniques adapted to every kind of exploitation exist. But the market prices are not adapted to sustainable processing. For example, an important argument in favour of AD is the production of energy. However the proceeds from the energy cover only at most 10 % of the operation costs, since comparable oil and electricity prices are much lower.

Advocates of a purely energetic exploitation of biowaste claim that composting is no more necessary. The woody fraction could be burnt in wood chips heating systems and the remainder anaerobically digested. This point of view overlooks the fact that without aerobic composting there is no compost to speak of since compost is defined as the product of aerobic degradation. Therefore, after the digestion process, a post-composting phase is mandatory. The sense of anaerobically processing agricultural biowaste with a high percentage of wood that cannot be easily separated out is still in dispute. It is however certain that, in the future, digestate will have to be matured aerobically to be marketable.

Recycling only makes sense when a market exists for its products [51] This means that green waste processing plants must produce marketable goods. Up till now, it is only after an increase in production that an outlet with minimum costs is sought out. If a technology is to acquire a practical value, there must be a demand for its products. There is a general need for market investigations *before* any production is initiated. As long as the waste producers continue to pay for treatment without any investigation being done on the product marketing side, inappropriate technical investments will continue to be made. The existing technology is good, but there is much to be gained in better defining to what end it is applied. For example, there is a latent demand for growth substrates with suppressive capacity towards seedling diseases, etc. Global knowledge of these techniques exist, but specific recipes have never been elaborated. Similarly, when biogas is used for electricity production, some 50 % of the energy is lost as waste heat. However, AD plants are practically never built on sites were this energy could be beneficially exploited.

These examples show that if the market prices also covered the production costs, it would be possible to approach zero waste levels, but this is not the case. The difference between the production costs of marketable goods and the market price for such goods must then be paid by waste taxes. However, if their treatment led to the production of marketable goods, these waste materials could then lose their status as waste.

4.3 Active Landfill Control and Stabilization of MSW

Saburo Matsui

Municipal solid waste (MSW) is worldwide mostly managed by landfilling without incineration. Only a limited number of countries and cities practice incineration followed by landfilling of the ash. Incineration of MSW has the advantage of reducing the bulk of MSW by oxidation of organic materials, whereas direct MSW landfilling shows very slow oxidation and reduction of organic materials followed by a very long time period of stabilization. Generally, if space for slow oxidation and reduction processes of MSW is available, all municipalities select this method. If space is limited, incineration of MSW is inevitable and advanced incineration technology and subsequent pollution control technology is required.

Developing countries generally have a low technology standard in the application of MSW incineration. In addition, MSW itself is not suited for incineration, due a low caloric value (energy content). There is, therefore, a need to develop improved methods of MSW landfilling in contrast to today’s conventional “sanitary landfills”. However, most developing countries practice so called “open dumping”, resulting in the generation of many pollution problems such as gas emissions, odor, waste water formation, or ground water pollution. Sanitary landfills can provide better solutions than open dumping reducing many of the problems, yet, there is still a potential for improvement.

A novel approach to solve the problems mentioned is called “Active Control Landfill and Stabilization Method (ACLSM)”. This introduces technologies such as a) odor control during landfill processes; b) methane collection after closure of the landfill site; c) enhanced landfill stabilization by sulfate-reducing bacteria which suppresses methane formation; d) ensuring the decrease of toxic pollutants in leachates from the landfill site. Methane collection as well as suppression of methane formation during the various stages of landfilling are important objectives regarding issues of global warming, i.e. the reduction of greenhouse gases [47]. Methane is a much stronger warming agent than carbon dioxide. Therefore, developing countries can contribute to the efforts to stop global warming by introducing ACLSM.

4.3.1 How to Proceed in ACLSM?

There are five stages of MSW landfill and stabilization processes, namely 1) landfilling process; 2) landfill closure; 3) methane collection; 4) stabilization enhancement by stimulating bacteria from the sulfur cycle; 5) completion of landfill process (Fig. 4.8).

Stage 1 - Landfilling process: What are major problems in stage 1 when the landfilling begins? Odorous gas is immediately generated and leachate treatment becomes necessary to reduce high BOD values and ammonia concentrations in the waste water. Odorous gas consists mainly of hydrogen sulfide. During decomposition of organic matter, sulfate is easily reduced to sulfide by sulfate-reducing bacteria. Sulfide formation is successfully inhibited by adding nitrate to the landfill (e.g. irrigation with nitrate solutions) and bacterial denitrification is easily stimulated. Denitrification activity (i.e. the formation of nitrogen gas) usually outcompetes sulfate reduction so that sulfide is not formed. As a consequence, landfill leachates must be aerobically treated by ammonia-oxidizing

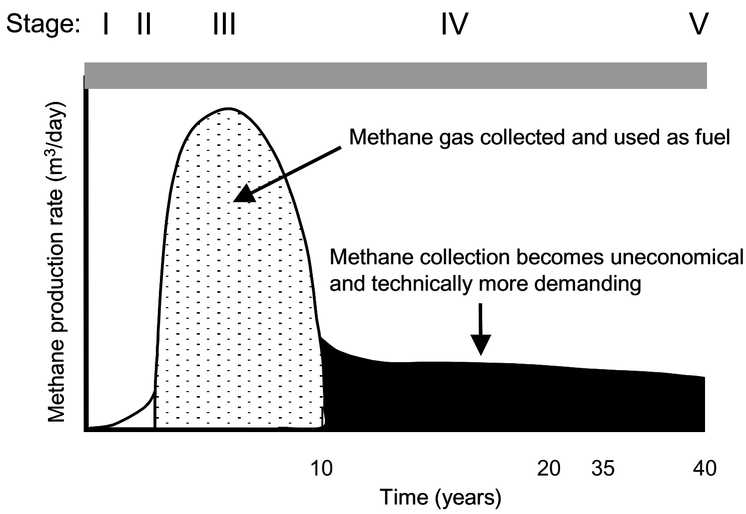

Fig. 4.8. Five stages of active control landfill and stabilization processes

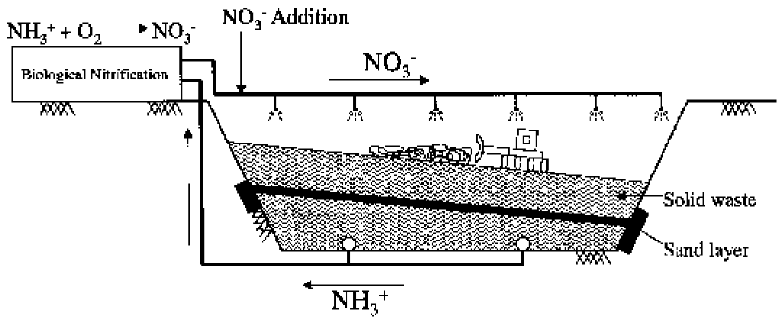

Fig. 4.9. Odor control by denitrification

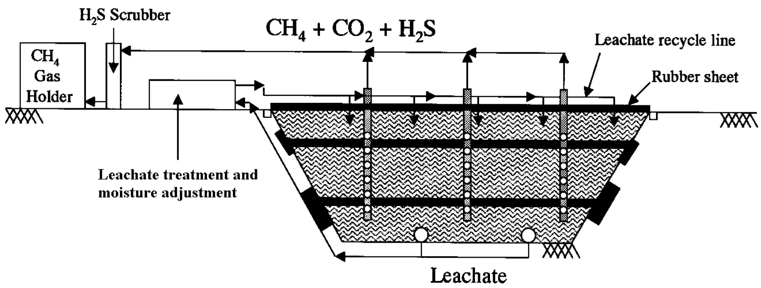

Fig. 4.10. Closure of the landfill site and collection of gaseous emissions

microorganisms. The leachate can be recycled and added back to the landfill where odorous gas control is accomplished (Fig. 4.9).

Stage 2 - Landfill closure: At stage 2, a landfill is sealed by covering the landfill site with a rubber or plastic sheet to prevent rain water seepage which is an important technique in the control of pollution problems. Additionally, gas can be collected from the site. Odorous gas (hydrogen sulfide) has to be eliminated by gas scrubbers and methane gas must be stored in a gas holders. Leachate treatment is one of the important control methods that require additional energy and financial expenditure [17]. If rain water seepage is controlled, leachate treatment costs are highly reduced. Treated leachates can be recycled to the site (Fig. 4.10).

Stage 3 - Methane collection: An important aspect is the collection of methane as biogas (fuel gas recovery for households). As an additional consequence, the proper management of MSW can also contribute to the reduction of greenhouse gases which contribute to global warming processes. This is of particular importance for developing countries.

Stage 4 - Stabilization enhancement by stimulating sulfate-reducing microorganisms: This stage lasts more than 40 or 50 years after the landfill closure, depending on the local climatic conditions of the site. It is very important to control methane emission during this stage. After a peak of high methane concentration during the first five years of stage 3 (Fig. 4.8), emission of low methane concentrations occurs for a very long time period. Due to the low concentrations, methane collection it is no longer economically beneficial. However, methane release (even at low concentrations) over an extremely long period has nonetheless an important impact on global warming. The solution to this problem is the introduction and stimulation of the microbial sulfur cycle in the active control landfill system: When leachate is recycled after aerobic treatment, the level of the sulfate concentration can be adjusted to approximately 1g per liter. Sulfate is the terminal electron acceptor for sulfate-reducing bacteria. Sulfate reducers can outcompete methane-forming bacteria, so that organic matter is degraded to organic acids while methane production is suppressed. As a result, hydrogen sulfide is formed. Organic acids are treated by aerobic bacteria during the leachate treatment process, which oxidize sulfide to sulfate. Sulfate originating from this process can be recycled and utilized when the landfill surface is irrigated with treated effluent. Hydrogen sulfide gas from deep landfill sites has to be oxidized by the aerobic soil filter covering the top of the landfill site. The top soil cover is approximately 1.5m deep and represents the habitat for sulfur-oxidizing bacteria (Fig. 4.11). Hydrogen sulfide rises from the bottom and is exposed to oxygen provided by air pumps at a depth of 1.5 m. Consequently, sulfide is biologically oxidized to sulfate or chemically oxidized to elemental sulfur within the soil filter. Basically, two main sulfur cycles have been established in the system, one being trough the landfill site and the leachate treatment, which is the major sulfur reduction and oxidation cycle, the other between the bottom of landfill and the landfill surface which might be a minor cycle. During the two sulfur flows being cycled, there is a slow build up of elemental sulfur in a landfill. The rubber or plastic sheet is placed over the biological soil filter in order to control the penetration of rain water and moisture level inside the landfill.

Stage 5 - Completion of landfill process: One of the major questions (especially for environmental engineers) is how to terminate the landfill process and how to re-use the landfill site for further purposes, such as agricultural or recreational use.

For this reason, the decomposition of degradable organic matter has to be complete. Although this is difficult to evaluate, there are some possible indicators: The occurrence of humic substances as well as some organic acids with trace phenol compounds which are basic elements of lignin polymers in leachate can indicate that the remaining organic matter is basically lignin and that any other degradable organic matter is present in only minor amounts [45, 47].

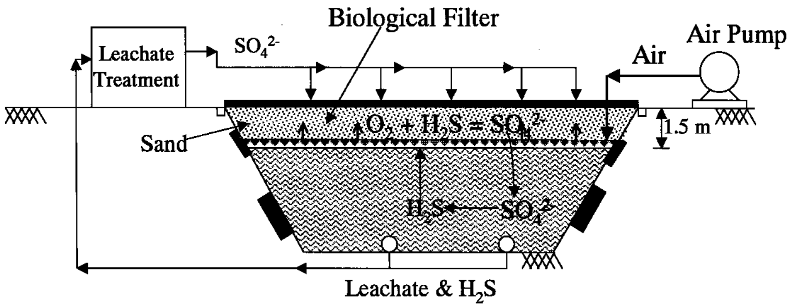

Fig. 4.11. Stabilization enhancement by stimulating the microbial sulfur cycle

Lignin is a natural polymer that cannot be degraded within a time span of several decades [30-32]. In addition, it is known that many synthetic chemicals are degraded by sulfate-reducing bacteria. Furthermore, most heavy metals, such as lead, cadmium, chromium, copper, zinc, aluminum, or iron, which are present in the various soluble forms, are finally stabilized in the form of metal sulfides.

4.3.2 Conclusions

Current landfill practices need improvement in many ways. ACLSM is a new approach for MSW management. Developing countries could introduce this approach where energy recovery as biogas can be extremely valuable and can contribute to the control of global warming efforts. There are many disadvantages in direct MSW landfilling practices: One typical case worth noting is the new landfill practice in Hanoi City, where the city introduced a standard MSW landfill method that had been developed based on Japanese experiences. As a major fatal mistake, the huge differences in MSW quality had not been considered. Japanese MSW is mostly incinerated, reducing the organic content and, consequently, decreasing methane and sulfide formation. The Japanese standard landfill technology does not provide much gas control measures because incineration of MSW is a premise. In contrast, Hanoi City MSW contained fractions rich in organic matter. This resulted in immediate odor problems as soon as landfilling activity started. Residents around the landfill site demonstrated against the activity and picketted in front of the landfill gate preventing the city from transporting MSW to the landfill site for three days. This issue was temporally settled by controlling sulfide emissions through chemical methods. The city is now considering changing the landfilling practice according to the MSW quality. Moreover, the leachate treatment facilities have not been established yet. Further problems are high BOD, COD, and elevated nitrogen as well as color formation in the leachate. The new technique has to provide odor control measures, leachate treatment, and toxic chemical management. Therefore, the introduction of active control landfill and stabilization processes in developing countries is strongly recommended.

4.4 Biotechnology for the Treatment of Inorganic Wastes

Helmut Brandl

4.4.1 Biogeochemical Element Cycles

It is an important prerequisite for future sustainable waste treatment technologies to integrate industrial civilization-dependent processes into natural element cycling. These technologies have to be oriented according to the natural biogeochemical cycles of elements found in the ecosphere, e.g. carbon, sulfur, or copper cycle. In nature, microorganisms are the driving force of the biogeochemical cycles. They show among all living creatures the highest biological diversity and represent the foundation of the biosphere. However, it is estimated that the vast majority of microorganisms is still not isolated, cultivated, and characterized [5]. As comparison, approximately 1.4 millions organismic species have been described until today, (Table 4.4): insects represent the group with the highest number of known species, whereas only a very small percentage of bacteria is known.

Microorganisms are of vital importance for the cycling of elements in the ecosphere, mainly either as primary producers (photosynthesis) or destruents (mineralization of organic matter). Figure 4.12 summarizes a general biogeochemical cycle driven by microorganisms. In a first step, carbon (as carbon dioxide) is utilized by primary producers (autotrophic microorganisms, plants) and biomass is formed by photosynthesis. The energy to drive this process is provided by the sun (light). Biomass is utilized by first order consumers (herbivores) which are themselves consumed by second order consumers (carnivores). Saprophytes (destruents) are responsible for the complete mineralization of organic matter (biomass, waste) formed by primary producers, herbivores or carnivores. Mineral

Table 4.4. Numbers of known organismic species in comparison to total estimated numbers

Organismic group	number of described species	estimated total number of species	percentage of known species
insects	950’000	8'000’000 - 100’000’000	1 - 12
plants	250’000	300'000 - 500'000	50 - 85
spiders	75’000	750’000 - 1'000’000	7.5 - 10
mollusks	70’000	200’000	35
fungi	70’000	1’000'000 - 1’500’000	5 - 7
vertebrates	45’000	50’000	90
protozoae	40’000	100’000 - 200’000	20 - 40
crustaceae	40’000	150’000	25
algae	40’000	200’000 – 10’000’000	0.4 - 20
viruses	5’000	500’000	1
bacteria	4’000	400’000 – 3'000’000	0.1 - 1

compounds are liberated and made available for primary producers. With this process the cycle is closed. In summary, the fundamental importance of microbial processes in the biogeochemical cycling is based on the ability of microorganisms to mobilize and convert elements [34].

Approximately 60 elements are involved in the turnover of the biosphere [34]. In completely closed biogeochemical cycles, elements are temporary immobilized in the biomass and subsequently recycled in relatively short time periods, whereas in incomplete cycles certain elements are immobilized in the hydro- or lithosphere for geological time spans.

Besides their fundamental importance in the mineralization and complete degradation of organic matter, microbes are naturally involved in the weathering of rocks, in the mobilization of metals from sulfidic minerals, in metal reduction and oxidation, in metal precipitation and deposition, and in isotope fractionation. These microbiological principles and processes might have the potential to be adapted for technical waste treatment applications. Besides the huge microbial potential to degrade a wide spectrum of organic substances (as known in composting or in the bioremediation of polluted soil), microbial abilities can also be used to cycle inorganic compounds (e.g. metals). Most of these capabilities are related to geological processes [19].

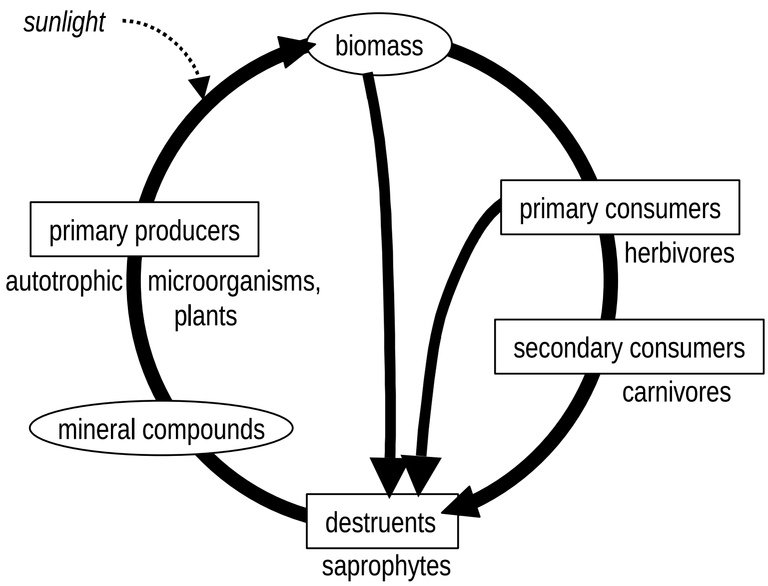

Fig. 4.12. General biogeochemical cycle driven by microorganisms both as primary producers for the formation of biomass and as destruents for the mineralization of biomass.

4.4.2 Organic Aspects: Mechanical-Biological Waste Pretreatment

Prior to final treatment (incineration, landfilling), municipal solid waste can be pretreated by mechanical-biological techniques. Microorganisms are involved in the transformation and degradation of the organic fraction of the waste. As alternative to thermal pretreatment (incineration in waste treatment plants) municipal solid waste is subjected to a combined mechanical and biological treatment to improve certain properties (e.g. stabilization) of waste fractions and to reduce the hazardous potential of the waste [58].

The first step of the treatment consist of a mechanical process. Municipal solid waste can be sorted, sieved, shredded, magnetically separated, and homogenized. As result, waste is classified in several fractions, namely reusable materials, a fraction of high calorific value, a heavy mineral fraction, and a fraction rich in organics, which is readily biodegraded [28]. The main goals of the mechanical treatment are the recovery of valuable and reusable components, the conditioning (volume reduction, particle size reduction, concentration of certain compounds) of the waste for an optimal subsequent biological or thermal treatment [35].

In a second step, a biological treatment under either oxic or anoxic conditions follows mechanical treatment. Under oxic conditions, the fraction rich in organic matter is composted in drums or bins as well as in tunnels or windrows requiring periodical agitation (turning) [28]. Most of the organic waste materials (agricultural and food industrial wastes, sewage sludge, etc) are composted in simple piles or prisms. These can be mechanically turned or undisturbed (static) prism, which are equipped with a built in aeration system. Fermentation under anoxic conditions requires a closed system where resulting gases (mainly methane) can be collected. The gas can be utilized for heating or as energy source (e.g. for cars). Consequently, the net energy gain from biogas formation is a major advantage of this technology [28]. Finally, residual fractions originating from the mechanical-biological pretreatment can be incinerated for volume reduction and energy recovery or disposed in landfills.

Landfilling of mechanical-biologically pretreated waste is mainly characterized by reduced volume, reduced gas and leachate emissions of environmentally hazardous compounds as well as a reduced settling behavior of the landfill [58]. Several goals are pursued with a mechanical-biological waste pretreatment [28]:

1. Reduction of landfill volume. As a result from separation and recycling of reusable waste fractions as well as from biological degradation of organic matter, the landfill volume is reduced by 30% after mechanical treatment and by 60% by a combined mechanical-biological treatment [28].
2. Reduction of the emission potential of landfill gas and leachate. In comparison to untreated municipal solid waste gas formation can be reduced by 75 to 90% resulting in gas emission rates of 20 to 40 m^3 per ton of dry matter [52]. During pretreatment, the main fraction of readily degradable organic compounds is decomposed under oxic conditions by microorganisms whereas recalcitrant substances remain in the landfill. Organic compounds include cellulose, non-

cellulose carbohydrates, proteins, lipids, and lignin. Cellulose is the compound which is easily degraded, lignin is the most-recalcitrant substance [52]. Long-term microbiological (and chemical) processes in the landfill are shortened to a few months by the mechanical-biological treatment [28]. Additionally, the organic load of landfill leachate is also reduced by up to 80% [28]. The acidic phase in the landfill is virtually eliminated because the organic material has been degraded prior to landfilling [52].

3. Reduction of deposit formation (incrustinations) in the leachate collection system [28].
4. Increase of the quality of the residual waste due to the removal and separation of contaminants and unwanted components.
5. Improving landfill operation due to dust reduction and odor emission [28].
6. Reduction of landfill settling. Mechanical-biological waste pretreatment also influences the physical behavior of the landfill. After separation of waste fraction with a high calorific value and a biological treatment for several months, landfill settlement is in the range of only 1% [52].

An ecological evaluation compared mechanical-biological waste treatment technologies with waste incineration regarding the effect on several environmentally relevant parameters [52]: It was demonstrated that both waste incineration and mechanical-biological pretreatment reduced the demand for fossil fuels only to a small extent. However, according to a recent study [52], waste incineration contributed to a decrease of the formation of summer smog whereas mechanical-biological waste pretreatment resulted in an increase. In contrast, mechanical-biological pretreatment was responsible for an enhanced ozone degradation. Contributions of both waste incineration and mechanical-biological pretreatment regarding global warming (greenhouse effect) was only of minor importance [52]. The study conducted in Germany concluded that the results obtained strongly depend on the local basic conditions regarding existing infrastructure and economical considerations. A generalization favoring either waste incineration or mechanical-biological waste pretreatment can hardly be deducted.

4.4.3 Inorganic Aspects: Microbe-Metal-Interactions

In addition to biotechnological processes regarding the transformation and degradation of organic compounds in municipal solid waste, microorganisms can also play an important role with respect to the portion of inorganic compounds (metals) in the waste: Metal-containing wastes can be biotechnologically treated to either recycle metal values from the waste or to remove unwanted metal-compounds resulting in an improvement of the waste quality.

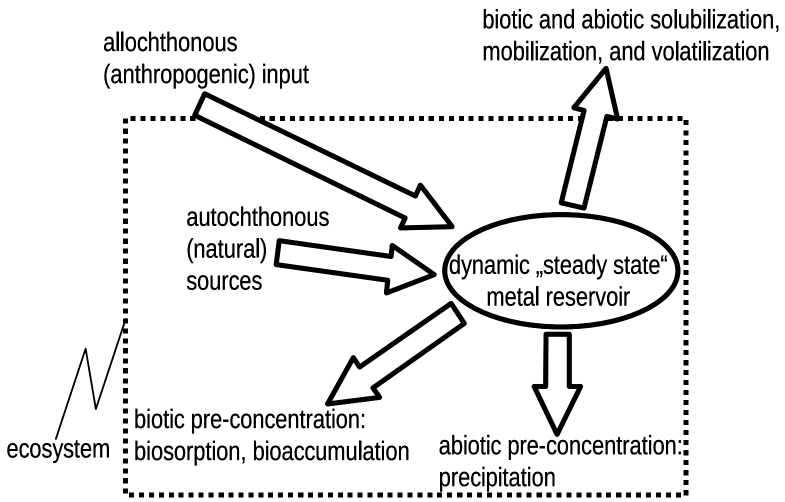

Fig. 4.13. Sources and sinks of metals in an ecosystem

Generally, it is assumed that a large fraction (>90%) of microbial populations is attached to particulate phases in environments where solid surfaces (e.g. mineral particles, biomass) are present. Particle-associated microbial populations are responsible for transformations of organic and inorganic substances. It is generally accepted that cells are not in direct contact with the solid surface, but they are surrounded by a layer of extracellular polymeric substances (EPS) which represent together with other compounds a complex matrix and are part of natural biofilms. This EPS layer can be several micrometers thick and fills the distance between the solid surface and the microbial cell.

Regarding the presence of mineral and metallic compounds in an ecosystem, several metabolic reactions (metal transformations) can occur when microbes are in contact with solid metals or metals in solution [6]. Metals are present in an ecosystem in a dynamic “steady state” reservoir (Fig. 4.13). This metal reservoir (pool) is supplied from either allochtonous or autochthonous sources. Allochthonous input includes anthropogenic activities such as industry, mining, or agriculture, whereas geogenic sources such as rock or soil are autochthonous (natural) metal sources. Simultaneously, metals are removed from this pool by biotic and abiotic processes (sorption, precipitation), are immobilized and remain in the ecosystem. By biotic or abiotic mobilization processes metals can also be remobilized and leave the ecosystem (Fig. 4.13). In natural environments, microbial cells are constantly exposed to stress conditions (presence of metals) and have, therefore, developed several mechanisms to overcome this pressure. Besides metal detoxification, microorganisms can also gain energy from some metal transformations (e.g. oxidation, reduction).

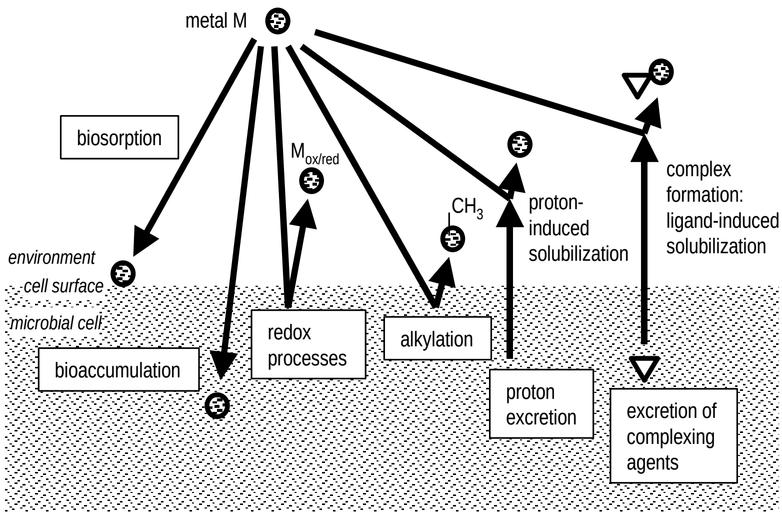

Fig. 4.14. Schematic presentation of possible mechanisms of microbe-metal-interactions

Figure 4.14 gives a schematic overview on possible reactions and mechanisms:

1. Metals can be concentrated by dead or living microbial biomass. Metal compounds are extracellularly bound onto cell surfaces and removed from an aqueous solution, a meachanism described as “biosorption”. Biosorption is defined as a passive process of metal sequestering and concentration by chemical sites naturally present and functional in biomass [57]. As a possibility, EPS layers act as sorbing site. EPS usually contain functional groups such as carboxyl, sulfonate, phosphate, hydroxyl, amino, or imino residues, which can interact with metal ions by their electrical charge. Generally, more than one functional group of the biomass is involved in biosorption, depending on the environmental conditions (e.g. pH, salinity), type of biomass, and the type of metal present [16]. Metal sorption can be more or less selective [57]. As example, it has been demonstrated that freeze-dried cells of cyanobacteria (*Synechococcus* sp.) can remove more than 98% of copper and lead, respectively, from an aqueous solution [26].
2. Soluble metals can be transported through the cell membrane by ion pumps, ion channels, or other carrier compounds and are accumulated within the cells. This process is termed “bioaccumulation”. In general, bacteria can sequester metals by an energy-consuming process involving the transport to the interior of the cell. As example, iron can be removed from the environment and be accumulated by specialized bacteria which have the ability to orient themselves in the earth magnetic field, a phenomenon called magnetotaxis. The metal is transported through the cell membrane and accumulated as solid particles (magnetosomes) in the cell plasma [55]. These magnetosomes are made of ferromagnetic mineral magnetite, but can contain also iron sulfides such as greigite, pyrrhotite, and pyrite. By the sequestering high concentrations of iron intracellularly as magnetite or iron sulfide, magnetotactic bacteria have an

important impact on their environment [55]. Another examples is the intracellular accumulation of silver crystals. *Pseudomonas stutzeri* is capable of forming nanocrystals of silver when growing in the presence of growth medium containing dissolved silver salts [33]. Most frequently, however, living cells store toxic metals in immobile and ineffective forms bound to high molecular-weight proteins.

3. During oxidation-reduction processes (also termed redox processes), metals can be microbially oxidized or reduced. From both reactions energy is provided for microbial growth. As result from the transformation, metal mobility is either decreased or increased depending on the type of metal and its oxidation state. In addition, certain metals such as cobalt, copper, iron, magnesium, manganese, molybdenum, or zinc are essential for the support of microbiological functions, e.g. as cofactors in metal-containing enzymes (metalloproteins).
   A variety of metals can be enzymatically reduced in metabolic processes which are not related to metal assimilation, a process described as dissimilatory metal reduction [40]. During the degradation and mineralization of organic matter, metals serve as terminal electron acceptor when alternatives (e.g. oxygen, nitrate) are absent. Iron(III) and manganese(IV) reduction is widespread in the microbial world. A series of microorganisms from mostly anoxic soils, sediments, or aquifers are known to couple metal oxidation of simple organic acids, alcohols, aromatic compounds, or hydrogen with the reduction of oxidized metal species [40]. Reduction of uranium, selenium, chromium, and mercury can also result in a metabolic energy gain, whereas the reduction of technetium, vanadium, molybdenum, gold, silver, and copper are investigated to a lesser extent and leave, therefore, some open questions on biochemical reactions.
   Contrasting reduction, metals can also microbially be oxidized to provide energy for growth and other vital metabolic processes [43]. Iron (II) oxidation is probably the best investigated case: A series of microorganisms are known to form ferric iron from metal-containing solids such as pyrite or arsenopyrite. These organisms, which are important for the biogeochemical cycling of iron, are mostly found in acidic environments (at pH values of 2 to 3) related to ore resources or mining sites [7]. Iron oxidizers are responsible for the generation of often extremely acidic effluents from ore mines (acidic mine drainage) which can pose severe environmental problems [42]. Microorganisms capable of oxidizing manganese (II) can be detected in metal-rich freshwater sediments [54]. It has been demonstrated that these organisms contribute significantly to the formation of certain types of ore.
4. Certain metals can be alkylated resulting in an increased metal mobility [56]. This process is described as “metal volatilization”. Metals can be emitted from ecosystems as gaseous compounds. Methylation is the best known alkylation process. A methyl group is enzymatically transferred to the metal and covalently bound. A series of metals and metalloids such as antimony, arsenic, cadmium, chromium, gold, lead, palladium, platinum, selenium, tellurium, thallium, and tin can be methylated [37]. However, some methylated metals,

e.g. lead and cadmium, show only a week stability in natural ecosystem, especially in the presence of light, oxygen, and water.

5. The microbial secretion of protons can result in changes of the metal mobility. Usually, metals are more mobile under acidic condition. The process is called "acidolysis" or proton-promoted metal solubilization. Under these conditions protons are bound to the surface resulting in the weekening of critical bonds as well as in the replacement of metal ions leaving the solid surface [24]. This is especially the case in the presence of metal oxides.
6. The microbial formation of complexing or chelating agents can lead to an increase of metal mobility, a mechanism termed "complexolysis" or ligand-promoted metal solubilization. On metal surfaces, complexes are formed by ligand exchange polarizing critical bonds and facilitating the detachment of metals species from the surface. Organic ligands (bi- or multidentate ligands) which are able to form surface chelates are particularly effective in solubilizing metals [24]. Oxalate and citrate – both very common microbial products formed by bacteria or fungi – belong to this group. A kinetic model of the coordination chemistry of mineral dissolution has been developed which describes both the dissolution of oxides by the protonation of the mineral surface as well as the surface concentration of suitable complex-forming ligands such as oxalate, malonate, citrate, and succinate [24]. Proton-promoted and ligand-promoted mineral solubilization occurs simultaneously in the presence of ligands under acidic conditions. It has been shown that dissolution rates coefficients increase with increasing numbers of ligand functional groups and can be predicted from the reactivities of aqueous ligand-metal complexes [41].
   Conversely, soluble metal species can also be immobilized (precipitated) by suitable complexing agents. Under anoxic conditions and in the presence of sulfate, sulfate-reducing bacteria form hydrogen sulfide as a final product which can react with soluble metals resulting in the formation of highly insoluble metal sulfides [8]. Metal sulfides show very low solubility products, so that metals are efficiently precipitated even at low sulfide concentrations [25]. Additionally, the activities of sulfate-reducing bacteria can result in a reduction of the acidity in an environment leading to the precipitation of metals as hydroxides, e.g. as copper and aluminum hydroxide [25].

In summary, mineralytic effects of bacteria and fungi on minerals are based mainly on three principles, namely acidolysis, complexolysis, and redoxolysis. As described earlier, microorganisms are able to mobilize metals by the formation of organic or inorganic acids (protons), by oxidation and reduction reactions; and by the excretion of complexing agents. Sulfuric acid is the main inorganic acid found in leaching environments. It is formed by sulfur-oxidizing microorganisms such as *Acidithiobacillus* species. A series of organic acids are formed by bacterial (as well as fungal) metabolism resulting in organic acidolysis, complex and chelate formation [3]. It has been suggested that a combination of all three mechanisms might be responsible for metal solubilization, termed "bioleaching" in the case of industrial applications. These microbial activities can be applied in the industry for the recovery of metals from solid materials. The technology has successfully found practical application in copper and gold mining (also termed “biomining”) where low-grade ores are biologically treated to obtain metal values which are not accessible by conventional (mechanical or thermal) treatments [9]. Metals can be obtained from leachates by suited techniques (e.g. precipitation, cementation, or electrowinning). Besides industrial interests, the application of bioleaching technologies must also be seen in the context of a sustainable future in which industrial technologies have to be increasingly in harmony with the global material cycles of the biosphere.

4.4.4 Biological Treatment of Heavy Metal Rich Wastes

In general, bioleaching is a process described as being "the dissolution of metals from their mineral source by certain naturally occurring microorganisms" or "the use of microorganisms to transform elements so that the elements can be extracted from a material when water is filtered trough it" (Atlas and Bartha 1997, Parker 1992). Additionally, the term "biooxidation" is also used [27]. Usually, "bioleaching" is referring to the conversion of solid metal values into their water soluble forms using microorganisms. In the case of copper, copper sulfide is microbially oxidized to copper sulfate and metal values are present in the aqueous phase. Remaining solids are discarded. "Biooxidation" describes the microbiological oxidation of host minerals which contain metal compounds of interest. As a result, metal values remain in the solid residues in a more concentrated form.

One of the first reports where leaching might have been involved in the mobilization of metals is given by the Roman writer Gaius Plinius Secundus (23 - 79 A.D.). In his work on natural sciences, Plinius describes how copper minerals are obtained using a leaching process. The Rio Tinto mines in South-Western Spain are usually considered as the cradle of biohydrometallurgy. These mines have been exploited since pre-Roman times for their copper, gold, and silver values. However, with respect to commercial bioleaching operations on an industrial scale, biohydrometallurgical techniques have been introduced to the Tharsis mine in Spain ten years earlier [49]. As a consequence to the ban of open air ore roasting and its resulting atmospheric sulfur emissions in 1878 in Portugal, hydrometallurgical metal extraction has been taken into consideration in other countries more intensely. In addition to the ban, cost savings were another incentive for the development: Heap leaching techniques were assumed to reduce transportation costs and to allow the employment of locomotives and wagons for other services.

Efforts to establish bioleaching to the Rio Tinto mines have been undertaken in the beginning of the 1890ies. Heaps (10 m in height) of low-grade ore (containing 0.75% Cu) were built and left for one to three years for "natural" decomposition [49]. 20 to 25% of the copper left in the heaps were recovered annually. It was calculated that approximately 200'000 tons of raw ore could be treated in 1896. Although industrial leaching operations were conducted at Rio

Tinto mines for several decades, the contribution of bacteria to metal solubilization was confirmed only in 1961, when *Thiobacillus ferrooxidans* (reclassified as *Acidithiobacillus)* was identified in the leachates. Earlier, in 1947, *Thiobacillus ferrooxidans* has already been identified as part of the microbial community found in acid mine drainage [14]. A first patent was granted in 1958 [59]. The patent describes a cyclic process where a ferric sulfate sulfuric acid lixiviant solution is used for metal extraction, regenerated by aeration (ferrous iron oxidation by iron oxidizing organisms), and re-used in a next leaching stage.

In addition to mining operations, biohydrometallurgy is also a promising technology useful either to recover valuable metals from industrial waste materials (e.g. slag, galvanic sludge, filter dust, fly ash) or to detoxify them for a less hazardous deposition. Biohydrometallurgical processing of solid waste allows the cycling of metals similar to biogeochemical metal cycles and diminish the demand for resources such as ores, energy, or landfill space.

As a case study, fly ash from municipal waste incineration (MSWI) represent a concentrate of a wide variety if toxic heavy metals (e.g. Cd, Cr, Cu, Ni). The low acute and chronic toxicity of fly ash for a variety of microorganisms and a low mutagenic effect of fly ash from MSWI has been demonstrated [38]. Nevertheless, the deposition of heavy metal containing material bears severe risks of spontaneous leaching of heavy metals due to natural weathering processes and due to uncontrolled bacterial activities [39]. In the light of Agenda 21 established at the Earth Summit in Rio in 1992 there is a strong demand to support sustainable development which include also the ecological treatment of waste and their safe disposal.

A biological metal leaching of fly ash is a very important step in this direction. To optimize the process, a semi-continuous laboratory-scale leaching plant (LSLP) was constructed in order to achieve high leaching efficiencies resulting in an increased overall load of elements in the effluent. In addition, treatment times were as compared to batch cultures [10]. A mixture of *Acidithiobacillus thiooxidans*, which forms high concentration of sulfuric acid due to bacterial energy metabolism, and *Acidithiobacillus ferrooxidans*, which is able to oxidize reduced metal compounds resulting in an increased solubility of these metals, is used to perform the leaching. However, biohydrometallurgical processing of fly ash poses severe problems especially at higher pulp densities, because of the high content of toxic metals and the saline and strongly alkaline (pH >10) environment [10]. By employing a semi-continuous process, higher pulp densities can be applied.

In a recent study, *Acidithiobacillus* species*, Pseudomonas putida, Bacillus megaterium,* and *Aspergillus niger* were used as test organisms and incubated with fly ash obtained from municipal waste incineration [36]. Elements such as cadmium, copper, or zinc were mobilized by >80% whereas others (e.g. Pb) were solubilized only by a small percentage (Fig. 4.5). The fungus *Aspergillus niger* proved especially effective for the leaching of Pb. Results show the potential of *Acidithiobacilli* together with different microorganisms to leach substantial quantities of toxic metals from fly ash.

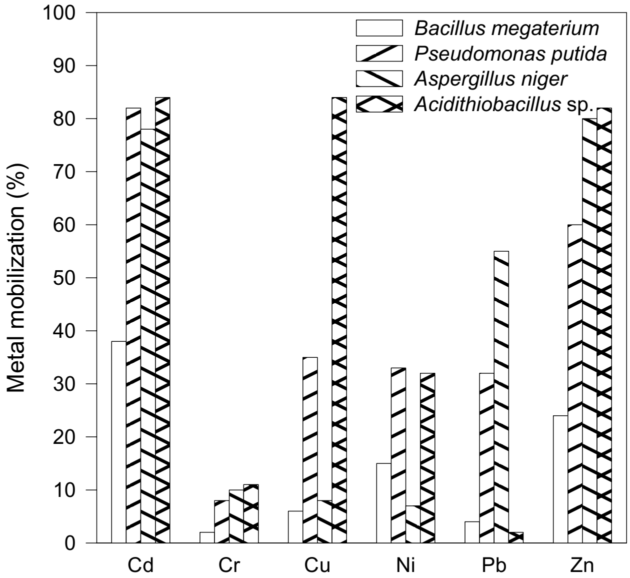

Fig. 4.15. Metal mobilization in a suspension of municipal waste incineration fly ash (20 g/l) by different microorganisms such as bacteria (*Bacillus megaterium, Pseudomonas putida*, *Acidithiobacillus* sp.) and a fungus (*Aspergillus niger*)

Table 4.5. Metal-containing solid wastes treated by biohydrometallurgical processes

material	source	metal content [g/kg]							
		Al	Cd	Cr	Cu	Ni	Pb	Sn	Zn
bottom ash	MSW incineration	46	tr	0.4	1.5	0.1	0.7	0.3	2.5
fly ash	MSW incineration	70	0.5	0.6	1	0.1	8	8	31
dust	electronic scrap	240	0.3	0.7	80	15	20	20	25
sludge	galvanic industries	nd	nd	26	43	105	nd	nd	166
soil	mining (Zn/Pb-mine)	nd	0.1	0.2	9	0.1	25	1.6	24
ore[a]	rock	300	0.1	300	2	7	4	10	10
soil[b]	earth crust	72	0.0003	0.1	0.03	0.04	0.02	0.01	0.05

nd not determined, *tr* traces

[a] metal concentration which makes a recovery economically interesting

[b] average metal concentration

Depending on the point of view, the mobilization or bioleaching of these metals could be either a hazard for the environment (leachates from landfills or ore deposits) or a chance to reduce toxic elements and to recover valuable metals by a low cost and low energy level technology compared with thermal treatment (e.g. vitrification or evaporation) [10]. The experimental installation described seems to be a first promising step on the way to a pilot plant with high capacities to detoxify fly ash (for a re-use of these materials for construction purposes) and for an economical recovery of valuable metals (e.g. zinc).

Slag and ash from municipal waste incineration represent concentrates of a wide variety of elements. Some metals (e.g. Al, Zn) are present in concentrations that allow an economical metal recovery, whereas certain elements (e.g. Ag, Ni, Zr) show relatively low concentrations (comparable to low-grade ores) what makes a conventional technical recovery difficult. Table 4.5 includes also other metal-containing waste materials having the potential to be treated microbiologically. Especially in these cases, where wastes contain only low amounts of metals, microbial processes are the technique of choice and basically the only possibility to obtain metal values from these materials.

A second case study reports the microbiological treatment of fine-grained residues originating from the mechanical recycling of used electric and electronic equipment [7]: Relatively short lifetimes of electrical and electronic equipment (EEE) result in the production of increased amounts of waste materials. In Switzerland, approx. 110,000 tons of electrical appliances have to be disposed yearly, while Germany these quantities are ten times bigger, reaching 1.5 million tons. Specialized companies are responsible for recycling and disposal of EEE which is dismantled and sorted manually. The resulting material is subjected to a mechanical separation process. Dust-like material is generated by shredding and other separation steps during mechanical recycling of electronic wastes: approx. 4% of the 2400 t of scrap treated yearly by a specialized company is collected as fine-grained powdered material. Whereas most of the electronic scrap can be recycled (e.g. in metal manufacturing industries), the dust residues have to be disposed in landfills or incinerated. However, these residues can contain metals in concentrations which might be of economical value. Provided that a suitable treatment and a recovery process is applied, this material might serve as a secondary metal resource. Results indicate that it is possible to mobilize metals from electrical and electronic waste materials by the use of microorganisms such as bacteria (*Acidithiobacillus thiooxidans, Acidithiobacillus ferrooxidans*) and fungi (*Aspergillus niger, Penicillium simplicissimum*). After a prolonged adaptation time, fungi as well as bacteria grew also at concentrations of 100 g/l [7]. Both fungal strains were able to mobilize Cu and Sn by 65%, and Al, Ni, Pb, and Zn by more than 95%. At scrap concentrations of 5 to 10 g/l *Thiobacilli* were able to leach more than 90% of the available Cu, Zn, Ni, and Al. Pb precipitated as lead sulfate while Sn precipitated probably as tin oxide. For a more efficient metal mobilization a two-step leaching process is proposed where biomass growth is separated from metal leaching. Metals were precipitated and recovered as hydroxides by the stepwise addition of sodium hydroxide.

4.4.5 Conclusions

Overall, it can be concluded that microbial metal mobilization can be applied for the recovery of metals from metal-containing solid wastes. It is possible to recycle the leached and recovered metals and to re-use them as raw materials by metal-manufacturing industries. Bioleaching represents a "clean technology" process on a low cost and low energy level compared with some conventional mining and waste treatment techniques. Government regulations and research policies that favor "green" technologies are a key incentive for developing such processes. These processes find a wide acceptance in public and in politics and represent innovative technologies with a proved market gap. However, the development of a process which is technically feasible and economically as well as ecologically justifiable is an important prerequisite.

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